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(54) Title: PHOTOGRAPHIC MATERIAL AND PROCESS (57) Abstract A novel blocked photographically useful compound element and process are based on a new blocking group that comprises a beta-ketocarbonyl group that is part of a 5- to 7-member heterocyclic ring containing a hetero-atom not adjacent to the beta-ketocarbonyl group. Such a blocked photographically useful compound provides a photographic material and process enabling more rapid release of the photographically useful group upon processing.		

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PHOTOGRAPHIC MATERIAL AND PROCESSBackground of the Invention

5 This invention relates to a new
photographic element containing a novel blocked
photographically useful compound that is capable of
more rapidly releasing the photographically useful
group of the compound upon photographic processing.

10 Various compounds, such as couplers and
dyes, are known in the photographic art that
contain a blocking group and that are capable of
being released or unblocked upon processing of the
photographic material containing the compound.
Such compounds and various blocking groups have
15 been described in, for example, U.S. Patents
4,690,885; 4,358,525 and 4,554,243 and U.S Patent
5,019,492. While these compounds have enabled
increased storage stability compared to compounds
that are not blocked and have provided release of
20 the photographically useful group from the compound
upon processing, often the stability of the
compounds during storage prior to exposure and
processing of the photographic materials containing
the compounds has not been entirely satisfactory
25 and the rate of release or unblocking of the
compound has been less than desired.

A continuing need has existed for a
blocked photographically useful compound containing
a blocking group that enables a means of tailoring
30 the ballasting of such compounds without adverse
effects upon a photographic material.

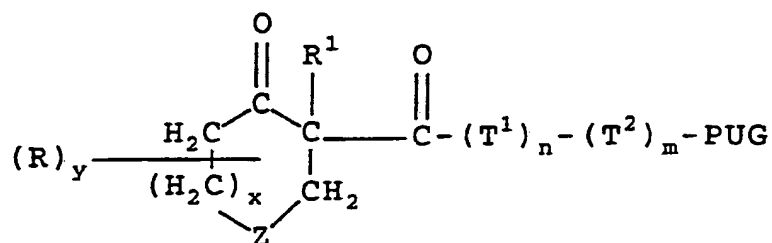
Summary of the Invention

The photographic element of the invention
comprises a support bearing at least one silver halide
35 photographic emulsion layer and a blocked
photographically useful compound comprising a

comprises a support bearing at least one silver halide photographic emulsion layer and a blocked photographically useful compound comprising a photographically useful group and a blocking group that is capable of releasing the photographically useful group upon processing the photographic element. The blocking group contains a beta-ketocarbonyl group that is part of a 5 to 7 member heterocyclic ring containing a nitrogen, sulfur, selenium or oxygen heteroatom located at a position not adjacent to the beta-ketocarbonyl group. The invention also encompasses the photographically useful compound and the photographic process employing the element.

Detailed Description of the Invention

A photographic element where the blocked photographically useful compound is represented by the formula:



wherein

T^1 and T^2 individually are releasable timing groups;

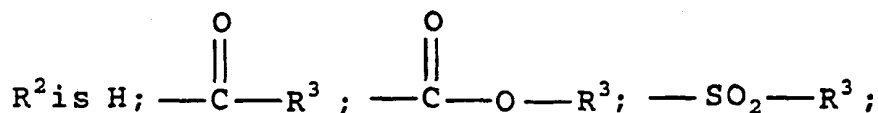
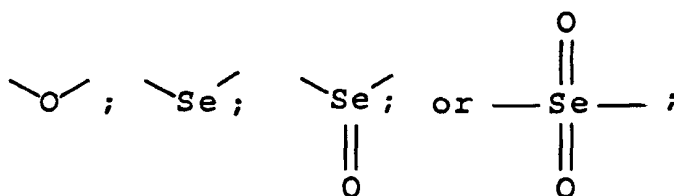
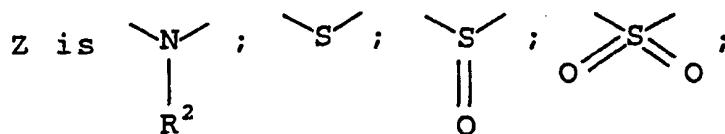
n and m individually are 0 or 1;

PUG is a photographically useful group;

x is 0, 1 or 2;

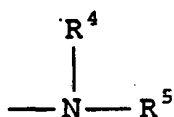
R^1 is unsubstituted or substituted alkyl;

Z is located at any ring position not adjacent to the ketocarbonyl group and;



substituted or unsubstituted alkyl or aryl or a
 5 photographic ballast group;

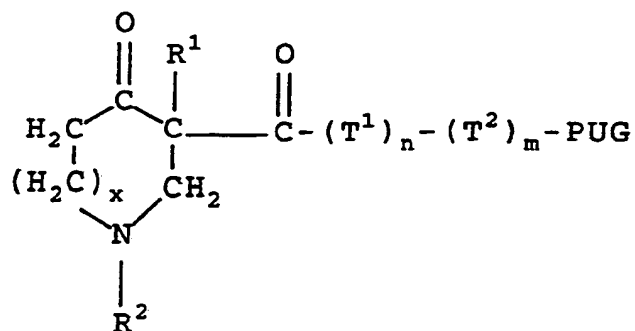
R^3 is unsubstituted or substituted alkyl, or
 aryl or



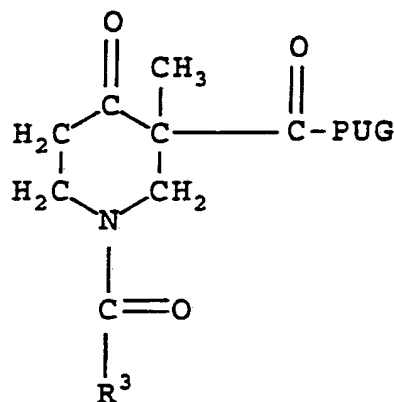
R^4 and R^5 individually are hydrogen, or
 10 unsubstituted or substituted alkyl, or aryl ;

R is substituted or unsubstituted alkyl or aryl
 or a photographic ballast group replacing a ring
 hydrogen; and Y is 0, 1, 2 or 3 represents a
 preferred embodiment of the invention.

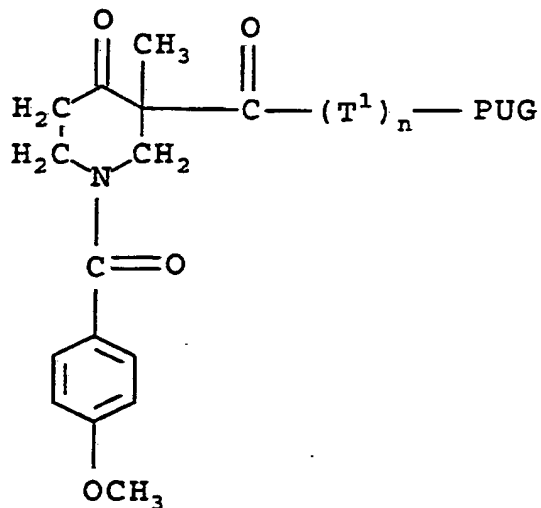
15 With the nitrogen hetero-atom, a preferred
 formula is:



and another formula is:

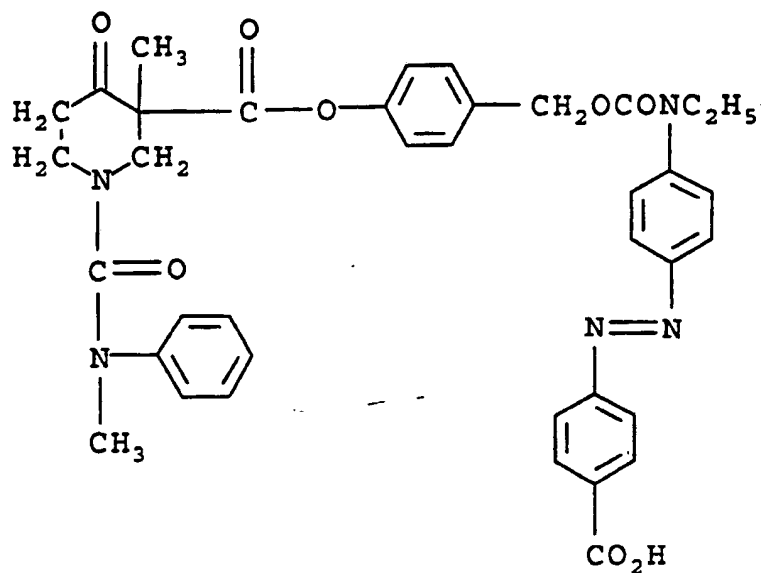


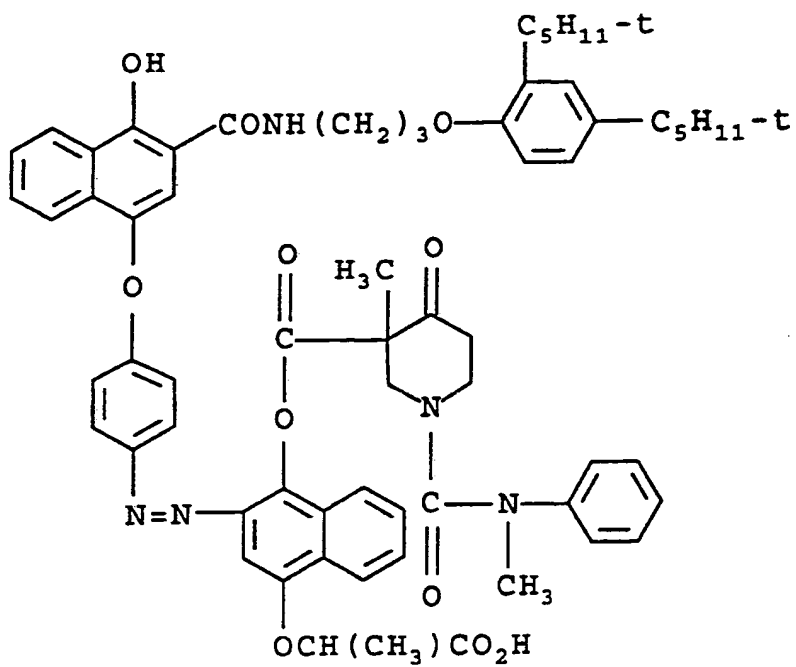
- 5 with further preferred blocked photographically useful compounds represented by the formula:



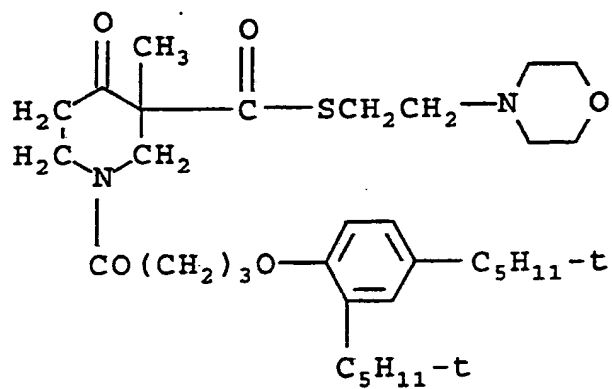
Examples of suitable blocked photographically useful compounds within the above

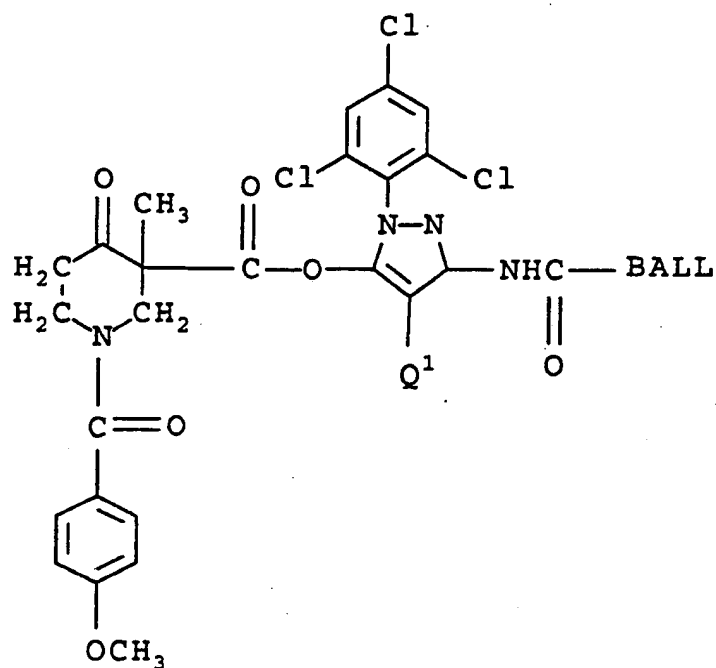
formula are represented by the formulas:



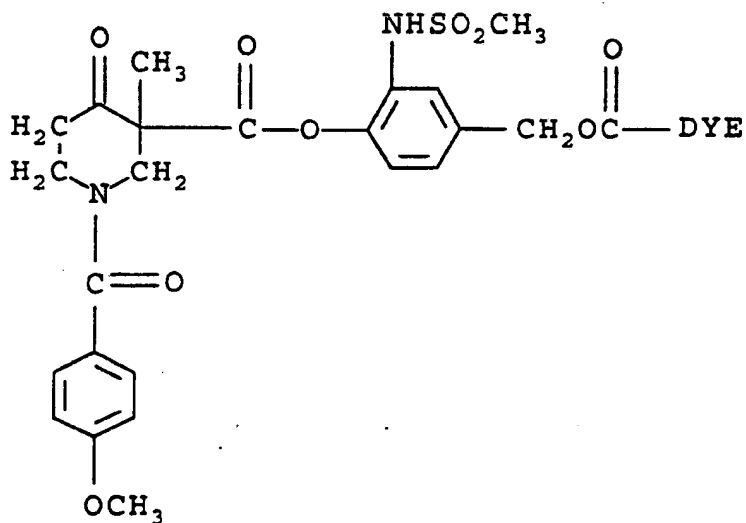


5





and



5

wherein

 Q^1 is hydrogen or a coupling-off group;

BALL is a ballast group; and

DYE represents the atoms completing a dye.

10

The blocking group as described can

contain a ballast group (BALL). Ballast groups known in the photographic art can be used for this purpose.

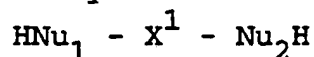
One embodiment of the invention is a
5 photographic element comprising a blocked
photographically useful compound containing the new
blocking group as described. Another embodiment is
a process of forming a photographic image by
developing an exposed photographic element as
10 described, preferably in the presence of a
dinucleophile reagent. A further embodiment is a
new photographically useful compound containing the
new blocking group as described.

The blocked photographically useful
15 compounds enable both excellent storage stability
and more rapid release upon processing of a
photographic element containing such a compound.
Both of these properties are achieved by the
blocked photographically useful compounds as
20 described due at least in part to the particular
structure of the new blocking group. The described
blocked photographically useful compounds react
only very slowly with nucleophilic compounds
containing one nucleophilic group, such as
25 methylamine, hydroxide or water, that help reduce
storage stability of the photographic element
containing such compounds. However, release occurs
very rapidly upon reaction with a nucleophilic
compound containing two nucleophile groups,
30 described herein as a dinucleophile reagent, such
as hydrogen peroxide and substituted and
unsubstituted hydroxylamines, hydrazines and
diamines. Moreover the described blocking group in
the blocked photographically useful compounds
35 enables more rapid release during photographic
processing, such as more rapid release than the

examples of blocked photographically useful compounds in U.S. Patent 5,019,492.

In chemical systems requiring the good storage properties and the more rapid release properties of the compounds as described, the release of the blocking group can be initiated by reaction of the blocking group with an appropriate dinucleophile reagent. Depending upon the particular photographically useful group, the particular blocking group and the desired end use of the compound, the initiation of deblocking can take place by reacting the particular dinucleophile reagent at concentrations and under conditions that enable the desired rate of release.

The dinucleophile herein means a compound represented by the formula:

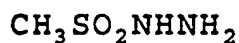
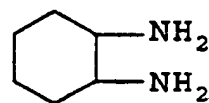
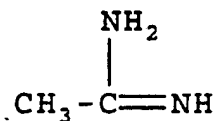
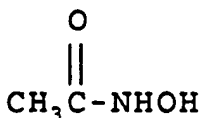
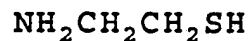
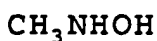
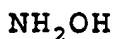
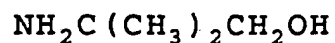
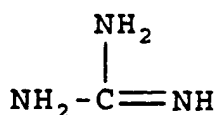
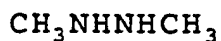
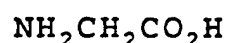
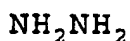
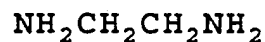


wherein Nu_1 and Nu_2 individually are nucleophilic N, O, S, P, Se, substituted nitrogen atoms, or substituted carbon atoms; X^1 is a chain of j atoms wherein j is 0, 1 or 2. Illustrative examples of useful dinucleophile reagents are as follows:

J=0:

J=1:

J=2:



Preferred dinucleophile reagents are hydroxylamine, hydrogen peroxide, and monosubstituted hydroxylamine. The dinucleophile reagent herein also includes a salt form of the reagent, such as the acid salts, for example, sulfate or bisulfite salts.

As used herein the term photographically useful group (PUG) refers to any group that can be used in a photographic material and that can be released from the blocking group as described. It refers to the part of the blocked photographically useful compound other than the blocking group and timing group(s). The PUG can be, for example, a photographic dye or photographic reagent. A photographic reagent herein is a moiety that upon release further reacts with components in the photographic element. Such useful photographically useful groups include, for example, couplers (such as, image dye-forming couplers, development inhibitor releasing couplers, competing couplers, polymeric couplers and other forms of couplers), development inhibitors, bleach accelerators, bleach inhibitors, inhibitor releasing developers, dye precursors, developing agents (such as competing developing agents, dye-forming developing agents, developing agent precursors, and silver halide developing agents), silver ion fixing agents, silver halide solvents, silver halide complexing agents, image toners, pre-processing and post-processing image stabilizers, hardeners, tanning agents, fogging agents, antifoggants, ultraviolet radiation absorbers, nucleators, chemical and spectral sensitizers or desensitizers, surfactants, and precursors thereof and other addenda known to be useful in photographic materials.

The PUG can be present in the photographi-

cally useful compound as a preformed species or as a precursor. For example, a preformed development inhibitor may be bonded to the blocking group or the development inhibitor may be attached to a timing group that is released at a particular time and location in the photographic material. The PUG may be, for example, a preformed dye or a compound that forms a dye after release from the blocking group.

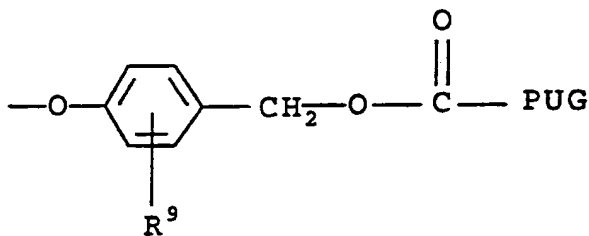
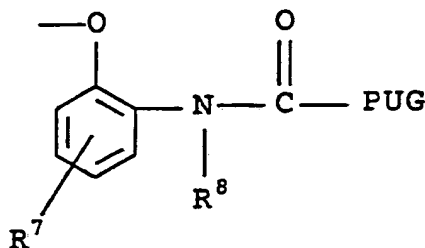
The photographically useful compound can optionally contain at least one releasable timing group (T) between PUG and the blocking group as described. The reaction of the photographically useful compound with a dinucleophile reagent can sequentially release the blocking group from the timing group and then the timing group can be released from the PUG. The term "timing group" herein also includes a linking group that involves little or no observable time in the release action. This can occur in, for example, the development step of an exposed photographic element when the developer composition comprises a dinucleophile reagent, such as a hydroxylamine. Any timing group that is known in the photographic art is useful as the timing group between PUG and the blocking group. Examples of useful timing groups are described in, for example, U.S. Patents 4,248,962 and 4,409,323 and European Patent Application 255,085.

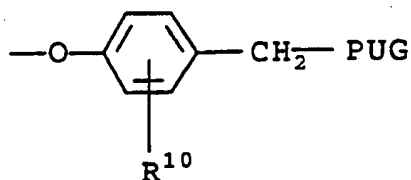
The particular timing groups employed, including the linkage by which they are attached to the PUG and the blocking group and the nature of the substituents on the timing group can be varied to help control such parameters as rate and time of bond cleavage of the blocking group and the PUG as well as diffusibility of the PUG and substituent

groups.

If the PUG is joined to the blocking group only through the timing group, then the cleavage of the bond between the timing group and the blocking group releases the timing group and the PUG as a unit. The particular timing group in this case can control the rate and distance of diffusion in the photographic material before the PUG is released from the timing group. The timing group should not contain a structure that inhibits the reaction of the blocking group with a dinucleophile reagent.

In the formulas as described timing groups T_1 and T_2 are independently selected to provide the desired rate and time of release of the PUG upon processing. The timing groups T_1 and T_2 can be the same or different. Examples of preferred timing groups for T_1 and T_2 are as follows:





wherein PUG is as described; and, R^7 , R^8 , R^9
 and R^{10} individually are hydrogen or substituents,
 5 such as alkyl, aryl, nitro, chloro and sulfonamido.

Other examples of useful timing groups are
 described in, for example, U.S. Patent 4,248,962
 and U.S. 4,772,537.

10 Illustrative examples of useful PUG's that
 can be blocked with the blocking groups as
 described are as follows:

I. Couplers:

A. Image Dye-Forming Couplers: Illustrative
 couplers include cyan, magenta and yellow image
 15 dye-forming couplers that are known in the
 photographic art. Illustrative cyan dye-forming
 couplers that can comprise the blocking group, as
 described include, for example, those described in
 U.S. Patents 2,772,162; 2,895,826; 3,002,836;
 20 3,034,892; 2,474,293; 2,423,730; 2,367,531;
 4,333,999; and 3,041,236. Illustrative magenta
 dye-forming couplers that can comprise the blocking
 group, as described include those described in, for
 example, U.S. Patents 2,600,788; 2,369,489;
 25 2,343,703; 2,311,082; 3,152,896; 3,152,896;
 3,519,429; 3,062,653; and 2,908,573. Illustrative
 yellow dye-forming couplers that can contain the
 blocking group, as described include those
 described in, for example, U.S. Patents 2,875,057;
 30 2,407,210; 3,265,506; 2,298,443; 3,048,194; and

3,447,928.

B. Illustrative couplers that form colorless products upon reaction with oxidized color developing agents and contain the blocking group, as described include those described in, for example, U.S. Patents 3,632,345; 3,928,041; 3,958,993; 3,961,959; and U.K. Patent No. 861,138.

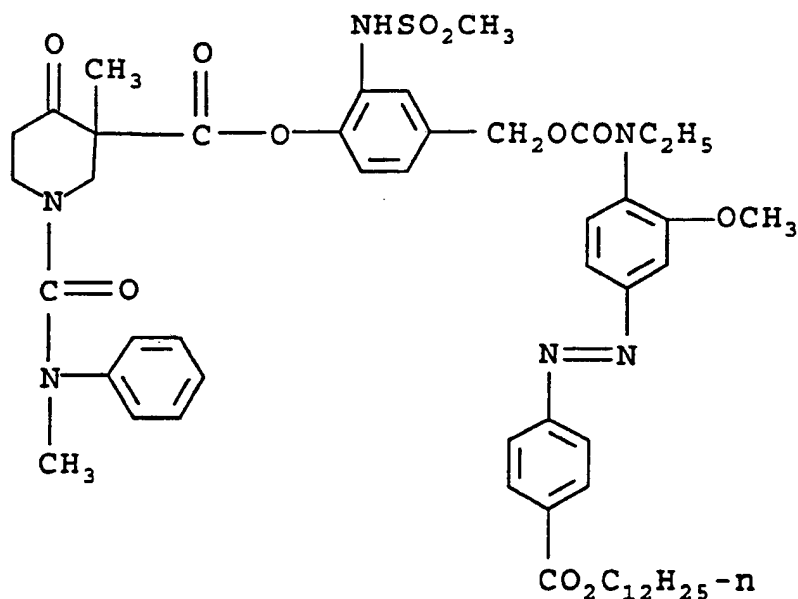
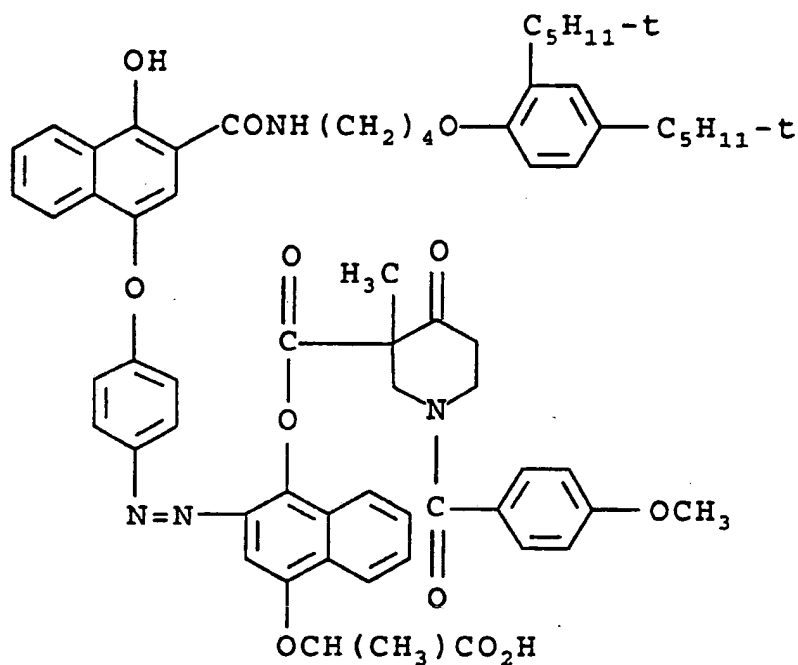
C. Illustrative couplers that form black dyes upon reaction with oxidized color developing agents and that can contain the blocking group, as described, include those described in, for example, U.S. Patents 1,939,231; 2,181,944; 2,333,106; and 4,126,461; German OLS No. 2,644,194 and German OLS No. 2,650,764.

D. Illustrative couplers that are development inhibitor releasing couplers (DIR couplers) and can contain the blocking group, as described, include those described in, for example, U.S. Patents 4,248,962; 3,227,554; 3,384,657; 3,615,506; 3,617,291; 3,733,201; and U.K. 1,450,479. Preferred development inhibitors as PUG's are heterocyclic compounds, such as mercaptotetrazoles, mercapto- triazoles, mercaptooxadiazoles, selenotetrazoles, mercaptobenzothiazoles, selenobenzothiazoles, mercaptobenzoxazoles, selenobenzoxazoles, mercaptobenzimidazoles, selenobenzimidazoles, benzotriazoles, benzodiazoles and 1,2,4-triazoles, mercaptothiadiazoles, tetrazoles, and imidazoles.

E. PUG's that are, or form, dyes upon release: Useful dyes and dye precursors include azo, azomethine, azopyrazolone, indoaniline, indophenol, anthraquinone, triarylmethane, alizarin, nitro, quinoline, indigoid, oxanol, and phthalocyanine dyes and precursors of such dyes, such as leuco dyes, tetrazolium salts or shifted

dyes. These dyes can be metal complexed or metal complexable. Representative patents describing such dyes are U.S. Patents 3,880,568; 3,931,144; 3,932,380; 3,932,381; and 3,942,987. Structures of illustrative dyes that can be blocked as described are as follows:

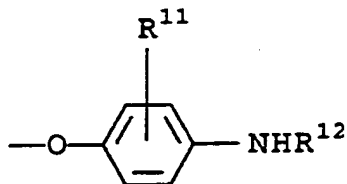
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F. PUG's that form developing agents:

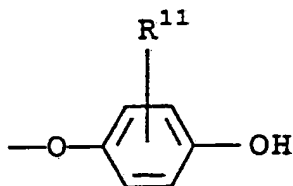
Developing agents released can be color developing agents, black-and-white developing agents and cross-oxidizing developing agents. They include aminophenols, phenylenediamines, hydroquinones and pyrazolidones. Representative patents describing such developing agents are U.S. Patents 2,193,015; 2,108,243; 2,592,364; 3,656,950; 3,658,525; 2,751,297; 2,289,367; 2,772,282; 2,743,279; 2,753,256; and 2,304,953.

Structures of preferred developing agents are:



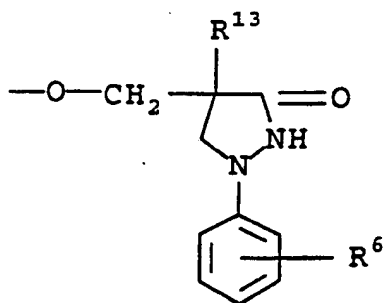
IIIID-1

where R¹² is hydrogen or alkyl of 1 to 4 carbon atoms and R¹¹ is hydrogen or one or more halogen (e.g. chloro, bromo) or alkyl of 1 to 4 carbon atoms (e.g. methyl, ethyl, butyl) groups and alkoxy.

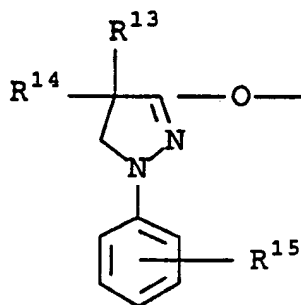


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where R¹¹ is as defined above.

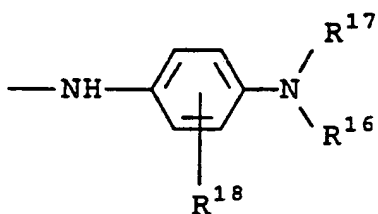


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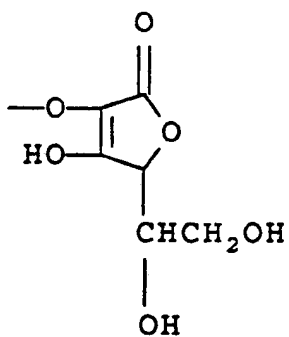


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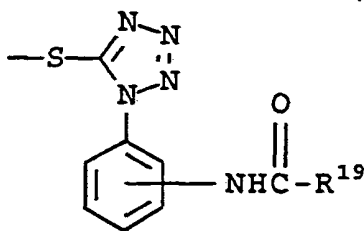
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10 where R^{15} is hydrogen or one or more alkyl, alkoxy or alkenedioxy groups of 1 to 4 carbon atoms and

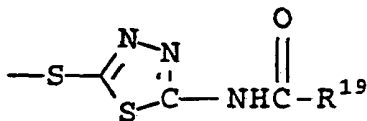
R^{13} , R^{14} , R^{16} , R^{17} and R^{18} individually are hydrogen, alkyl of 1 to 4 carbon atoms (e.g. methyl, ethyl) lower hydroxyalkyl of 1 to 4 carbon atoms (e.g. hydroxymethyl, hydroxyethyl) or lower sulfoalkyl.

G. PUG's that are bleach inhibitors:

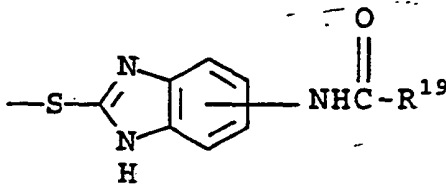
Representative bleach inhibitors that can be blocked as described include the illustrative bleach inhibitors described in, for example, U.S. Patents 3,705,801; 3,715,208 and German OLS No. 2,405,279. Structures of illustrative bleach inhibitors are:



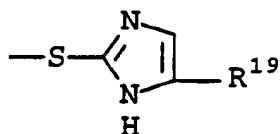
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IIIIE-2



IIIIE-3



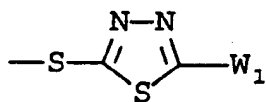
IIIIE-4

where R^{19} is an alkyl group of 6 to 20 carbon atoms.

H. PUG's that are bleach accelerators:

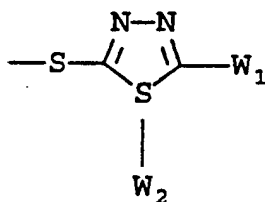
5

Representative bleach accelerators that can be blocked as described include the illustrative bleach accelerators represented by the following structures:

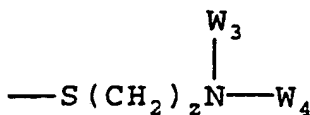


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IIIF-1

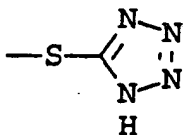


IIIF-2

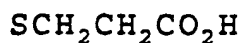


15

IIIF-3



IIIF-4



IIIF-5

20

wherein W_1 is hydrogen, alkyl, such as ethyl and

butyl, alkoxy, such as ethoxy and butoxy, or alkylthio, such as ethylthio and butylthio, for example containing 1 to 6 carbon atoms, and which may be unsubstituted or substituted; W₂ is hydrogen, alkyl or aryl, such as phenyl; W₃ and W₄ are individually alkyl, such as alkyl containing 1 to 6 carbon atoms, for example ethyl and butyl or together can form a ring, such as morpholino; z is 1 to 6.

Other PUG's as described in the photographic art can also be blocked with a blocking group as described.

The blocked photographically useful compounds as described can be used in photographic materials and in ways that blocked photographic compounds have been used in the photographic art.

For example, the blocked photographic couplers can be incorporated in photographic elements and/or photographic processing compositions, such that upon development in the presence of a dinucleophile reagent the exposed photographic element and coupler will be in reactive association with oxidized color developing agent. When incorporated in a photographic element, the coupler compounds should as a rule be non-diffusible, that is they should be of such molecular size and configuration that they will not significantly diffuse or wander from the layer in which they are coated.

Photographic elements of the invention can be processed by conventional techniques in which color forming couplers and color developing agents are incorporated in separate processing solutions or compositions or in the photographic element. Option- ally, blocked color developing agents can be incorporated in the photographic element and simplified processing solutions used for processing

the element.

5 The photographic elements can be single color elements or multicolor elements. Multicolor elements contain dye image-forming units sensitive to each of the three primary regions of the visible spectrum. Each unit can be comprised of a single emulsion layer or of multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of the image-forming units, can be arranged in various orders as known in the photographic art. In an alternative format, the emulsions sensitive to each of the three primary regions of the spectrum can be disposed as a single segmented layer, such as by the use of microvessels as described in U.S. Patent 15 4,362,806.

20 A typical multicolor photographic element comprises a support bearing a cyan dye image-forming unit comprising at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, a magenta dye image-forming unit comprising at least one green-sensitive silver halide emulsion layer having associated therewith at least one magenta dye-forming coupler, and a yellow dye image-forming unit comprising at least one yellow dye-forming coupler. The element can contain added layers, such as filter layers, interlayers, overcoat layers, subbing layers, and the like.

30 The blocked photographically useful compounds as described can be present in and/or associated with one or more of the layers of the photographic element. The compounds can be in an emulsion layer and/or in an adjacent layer.

35 In the following discussion of materials useful in the emulsions and elements of the

invention, reference will be made to Research Disclosure, December 1978, Item No. 17643, and Research Disclosure, December 1989, Item No. 308119, published by Industrial Opportunities Ltd., Homewell Havant, Hampshire, PO9 1EF, U.K., the disclosures of which are incorporated herein by reference. These publications will be identified hereinafter by the term "Research Disclosure".

The silver halide emulsions employed in the elements can be comprised of silver bromide, silver chloride, silver iodide, silver chlorobromide, silver chloroiodide, silver bromoiodide, silver chlorobromoiodide or mixtures thereof. The emulsions can include coarse, medium or fine silver halide grains. High aspect ratio tabular grain emulsions are specifically contemplated, such as those described by Wilgus U.S. Patent 4,434,226, Daubendiek et al U.S. Patent 4,414,310, Wey U.S. Patent 4,399,215, Solberg et al U.S. Patent 4,433,048, Mignot U.S. Patent 4,386,156, Evans et al U.S. Patent 4,504,570, Maskasky U.S. Patent 4,400,463, Wey et al U.S. Patent 4,414,306, Maskasky U.S. Patents 4,435,501 and 4,643,966 and Daubendiek et al U.S. Patents 4,672,027 and 4,693,964. Also specifically contemplated are those silver bromoiodide grains with a higher molar proportion of iodide in the core of the grain than in the periphery of the grain, such as those described in GB 1,027,146; JA 54/48,521; US 4,379,837; US 4,444,877; US 4,665,012; US 4,686,178; US 4,565,778; US 4,728,602; US 4,668,614; US 4,636,461; EP 264,954. The silver halide emulsions can be either monodisperse or polydisperse as precipitated. The grain size distribution of the emulsions can be controlled by silver halide grain separation

techniques or by blending silver halide emulsions of differing grain sizes.

Sensitizing compounds, such as compounds of copper, thallium, lead, bismuth, cadmium and Group VIII noble metals, can be present during precipitation of the silver halide emulsion.

The emulsions can be surface-sensitive emulsions, that is, emulsions that form latent images primarily on the surfaces of the silver halide grains, or internal latent image-forming emulsions, that is, emulsions that form latent images predominantly in the interior of the silver halide grains. The emulsions can be negative-working emulsions, such as surface-sensitive emulsions or unfogged internal latent image-forming emulsions, or direct-positive emulsions of the unfogged, internal latent image-forming type, which are positive-working when development is conducted with uniform light exposure or in the presence of a nucleating agent.

The silver halide emulsions can be surface sensitized. Noble metal (e.g., gold), middle chalcogen (e.g., sulfur, selenium, or tellurium), and reduction sensitizers, employed individually or in combination, are specifically contemplated. Typical chemical sensitizers are listed in Research Disclosure, Item 17643, cited above, Section III and Research Disclosure, Item 308119, cited above.

The silver halide emulsions can be spectrally sensitized with dyes from a variety of classes, including the polymethine dye class, which includes the cyanines, merocyanines, complex cyanines and merocyanines (i.e., tri-, tetra-, and poly- nuclear cyanines and merocyanines), oxonols, hemioxonols, styryls, merostyryls, and streptocyanines. Illustrative spectral sensitizing dyes

are disclosed in Research Disclosure, Item 17643, cited above, Section IV and in Research Disclosure Item No. 308119, cited above.

5 Suitable vehicles for the emulsion layers and other layers of elements of this invention are described in Research Disclosure Item 17643, Section IX, and Research Disclosure, Item No. 308119, and the publications cited therein.

10 In addition to the couplers described herein the elements of this invention can include additional couplers as described in Research Disclosure, Item No. 17643 Section VII, paragraphs D, E, F and G and Research Disclosure Item No. 308119, and the publications cited therein. These
15 additional couplers can be incorporated as described in Research Disclosure, Item No. 17643, Section VII, paragraph C and Research Disclosure, Item No. 308119, and the publications cited therein.

20 The photographic elements as described can contain brighteners (Research Disclosure Item No. 308119, Section V), antifoggants and stabilizers (Research Disclosure Item No. 308119, Section VI), antistain agents and image dye stabilizers
25 (Research Disclosure Item No. 308119, Section VII, paragraphs I and J), light absorbing and scattering materials (Research Disclosure Item No. 308119, Section VIII), hardeners (Research Disclosure Item No. 308119, Section X), coating aids (Research
30 Disclosure Item No. 308119, Section XI), plasticizers and lubricants (Research Disclosure Item No. 308119, Section XII), antistatic agents (Research Disclosure Item No. 308119, Section XIII), matting agents (Research Disclosure Item No.
35 308119, Section XVI) and development modifiers (Research Disclosure Item No. 308119, Section XXI).

The photographic elements can be coated on a variety of supports as described in Research Disclosure Item No. 308119, Section XVII and the references described therein.

5 Photographic elements can be exposed to actinic radiation, typically in the visible region of the spectrum, to form a latent image as described in Research Disclosure Item No. 308119, Section XVIII and then processed to form a visible
10 dye image as described in Research Disclosure Item No. 308119, Section XIX. Processing to form a visible dye image includes the step of contacting the element with a color developing agent to reduce developable silver halide and oxidize the color
15 developing agent. Oxidized color developing agent in turn reacts with the coupler to yield a dye.

 Preferred color developing agents are p-phenylene diamines. Especially preferred are 4-amino-3-methyl-N,N-diethylaniline hydrochloride, 4-
20 amino-3-methyl-N-ethyl-N- δ -(methanesulfonamido)-ethylaniline sulfate hydrate, 4-amino-3-methyl-N-ethyl-N- δ -hydroxyethylaniline sulfate, 4-amino-3- δ -(methanesulfonamido)ethyl-N,N-diethylaniline hydrochloride and 4-amino-N-ethyl-N-(2-methoxy-
25 ethyl)-m-toluidine di-p-toluene sulfonic acid.

 With negative-working silver halide, the processing step described above provides a negative image. The described elements are preferably processed in the known C-41 color process as
30 described in, for example, the British Journal of Photography Annual of 1988, pages 196 -198. To provide a positive (or reversal) image, the color development step can be preceded by development with a non-chromogenic developing agent to develop
35 exposed silver halide, but not form dye, and then uniformly fogging the element to render unexposed

silver halide developable. Alternatively, a direct positive emulsion can be employed to obtain a positive image.

5 Development is followed by the conventional steps of bleaching, fixing, or bleach-fixing, to remove silver or silver halide, washing, and drying.

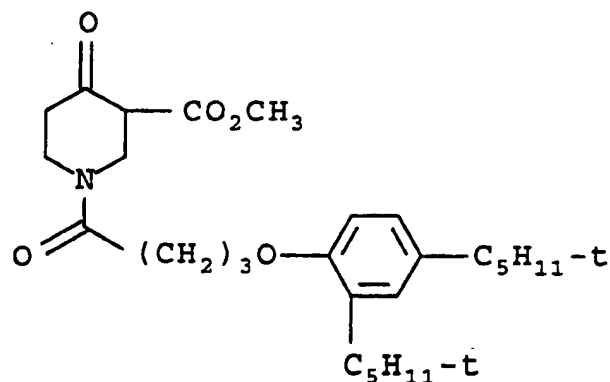
10 In processing it is preferable that the described dinucleophile reagent, such as a hydroxylamine, be present in the processing solution that is to be used to release or unblock the blocked photographically useful compound at the time desired. The concentration of the
15 dinucleophile reagent in the processing solution can vary depending on such factors as the particular processing solution components, the particular dinucleophile reagent, the processing time and temperature, the particular photographic element to be processed, the desired image and the
20 like. When the dinucleophile reagent is present in a color developer solution, the concentration of the dinucleophile reagent is typically within the range of 10^{-5} moles to 1 mole per liter of solution.

25 The blocked photographically useful compounds as described can be prepared by methods and steps known in the organic compound synthesis art.

30 A typical method of preparing a blocked photographically useful compound is as follows:

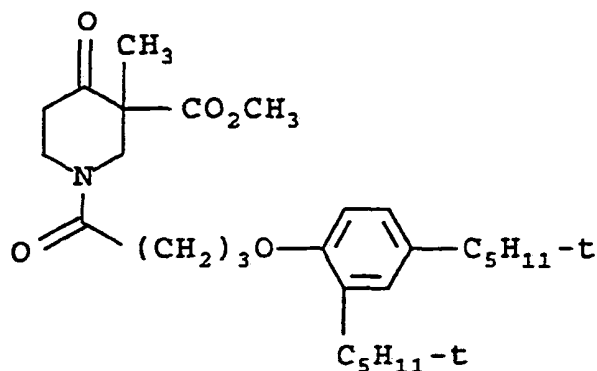
Synthesis I:

Preparation of:



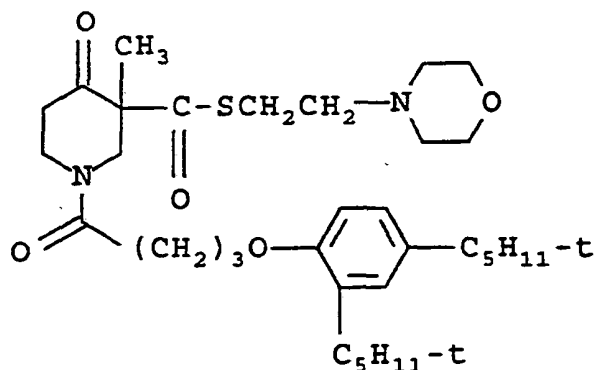
To a mechanically-stirred solution of 20g of methyl 4-oxo-3-piperidine carboxylate hydrochloride dissolved in 100 ml of water was added 12g of potassium bicarbonate. After complete dissolution of the solid, a solution of 35g of 4-(2,4-di-tert-amylphenoxy) butyryl chloride dissolved in 100 ml of ligroin (bp 35-50) was added. While stirring vigorously, an additional 10g of solid potassium bicarbonate was added. After stirring for one hour, the layers were separated. The organic layer was sequentially treated with 5% aqueous hydrochloric acid, water, and saturated aqueous sodium chloride solution. After drying over solid anhydrous sodium sulfate, the solvent was evaporated from the organic layer to give 49g of product as a light gold oil. The ¹H NMR spectrum was consistent with the desired structure.

Preparation of:



A well stirred mixture of 49g of the above material, 40g of cesium carbonate, 50 mL of iodomethane, and 250 mL of acetone was held at reflux for one hour. After cooling to room temperature, the reaction mixture was filtered to remove solid. The resulting oil was re-dissolved in diethyl ether and dried over solid anhydrous sodium sulfate. Filtration and evaporation of solvent gave 49g of gold oil. ¹H NMR was consistent with the desired structure. Mass spectral analysis was also consistent. By silica gel thin layer chromatography, the product had R_f=0.71 using 50/50 diethyl ether/ligroin(bp 35-50) as eluent.

Preparation of:



To a stirred solution of 18g of the above alkylated methyl ester in 150 mL of methylene

chloride under nitrogen was added cautiously 4mL of boron tribromide. After stirring for 15 minutes, 50 mL of water was added slowly. The reaction was stirred for 5 minutes, and then the layers were separated. The organic layer was dried over anhydrous sodium sulfate. After removing the solid by filtration, the filtrate was treated with 10 mL of oxalyl chloride overnight. The next day, the solvent was removed by evaporation. The residual oil and 5.5 grams of 2-morpholinoethanethiol were dissolved in 200 mL of methylene chloride. To this stirred solution was added 5.5 mL of triethylamine. After stirring for 3 days, the volatiles were removed by evaporation. The residue was stirred with diethyl ether and then filtered to remove undissolved solid. The evaporated residue was chromatographed on silica gel using 20/80 diethyl ether/methylene chloride to isolate the product having $R_f=0.33$ (same solvent system). 1H and ^{13}C NMR spectra were consistent with the proposed structure. Mass spectral analysis was also consistent. By this method, 2g of thiol ester was made.

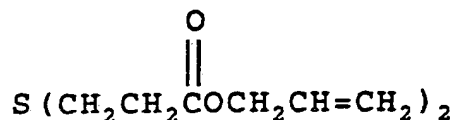
Synthesis II

Preparation of blocked compounds with sulfur heteroatom:

A solution of 100g of 3,3'-thiodiproionic acid, 120ml of allyl alcohol, 0.5g of para-toluenesulfonic acid monohydrate, and 100ml of toluene was heated at reflux for 10hr. with azeotropic removal of water. After cooling to room temperature, the organic phase was washed with saturated aqueous sodium bicarbonate solution, and the layers separated. The organic layer was dried over anhydrous sodium sulfate, filtered, and evaporated to give 146g of the desired diallyl

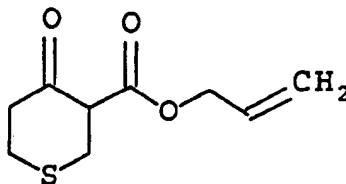
ester of structure S-1 as a gold oil. ¹H NMR (CDC13) 6.1-5.6 (m, 2H), 5.4-5.0 (three broad peaks, 4H), 4.5 (d, 4H), and 2.9-2.4 (m, 8H). A trace of toluene was also present. This material was suitable as is for future use.

COMPOUND S-1



To a stirred suspension of 45g of an 80% dispersion of sodium hydride in oil under nitrogen in 600ml of dry tetrahydrofuran was added linearly over a period of 4hr., 120g of allyl alcohol. After stirring for 1hr, 240g of the previously prepared diallyl ester was added linearly over a period of 4hr. The reaction was then taken to reflux and held for 4hr. After cooling to room temperature, 120g of acetic acid was linearly added over a period of 4hr. The precipitated solid is removed via Celite-aided filtration. The evaporated residue is passed through silica gel using 5% ether/ 95% ligroin (bp 30-60) as eluent to give 115g of the desired beta-ketoester of structure S-2 as a clear oil. (R_f=0.44 on silica gel using 10% ether/ 90% ligroin (bp 30-60)) ¹H NMR (CDC13): 12.3 (s, 2/3 H), 5.9-5.5 (m, 1H), 5.3-5.0 (m, 2H), 4.6 (d, 2H), 3.2 (s, 2H), 2.6 (t, 2H), and 2.5 (t, 2H).

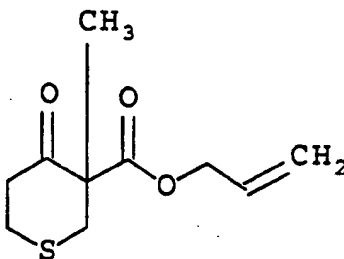
COMPOUND S-2



While stirring a suspension of 60g of potassium
5 t-butoxide in 1000ml of dry tetrahydrofuran under
nitrogen, 100g of the unalkylated beta-ketoester was
added linearly over a period of 50 minutes. The reaction
was then heated to reflux. While at reflux, 70g of
iodomethane was added linearly over a period of 35
10 minutes. After a period of 10 minutes at reflux, 20 g of
additional iodomethane was added linearly over a period
of 10 minutes while the reaction was still at reflux.
The 10 minute reflux period followed by the 10 minute
addition period of iodomethane was repeated 2 additional
15 times. The reaction was then held at reflux for 2hr. and
cooled to room temperature. After Celite-aided
filtration, the evaporated residue was passed through
1.5kg of silica gel using 5% ether / 95% ligroin (bp 30-
60) as eluent to give 45g of methylated beta-ketoester of
20 structure S-3 as a clear oil. (Rf=0.29 on silica gel
using 10% ether / 90% ligroin (bp 30-60)). ¹H NMR
(CDC13): 6.0-5.8 (m, 1H), 5.3-5.2 (m, 2H), 4.6 (d, 2H), 3.3
(doublet of doublets, 1H), 3.0-2.6 (m, 5H), and 1.4
(s, 3H).

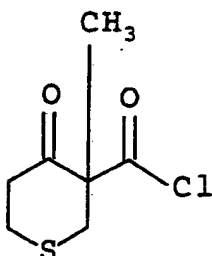
25

COMPOUND S-3



To a stirred suspension of 16g of methylated beta-ketoester and 15g of tetramethylammonium acetate in 250mL of dichloromethane and 50mL of tetrahydrofuran was added 0.5g of tetrakis(triphenylphosphine) palladium. The reaction was stirred under nitrogen in the absence of light for 0.5hr. To the thick suspension was cautiously added 10ml of oxalyl chloride in very small portions. Foaming was allowed to subside between additions. After stirring for 0.5hr, the volatiles were removed by rotary evaporation. An additional 100ml of fresh dichloromethane was added, and the volatiles were again removed. The residue was assumed to contain the desired acid chloride of structure S-4 and was used as is to make derivatives. The acid chloride was then reacted with the corresponding chloride of the desired photographic group to yield the finished blocked group in the same manner as in synthesis I.

COMPOUND S-4



In chemical systems that require a blocked reagent, the reagent can be released by reaction with a dinucleophile reagent. The reagent can be released by any dinucleophile reagent that is compatible with the particular chemical system. Selection of an optimum dinucleophile reagent and a particular blocked reagent will depend upon the particular chemical system, the desired end use of the blocked reagent, the particular conditions used for release. The blocking group can be as

described in such blocked reagents.

The following examples further illustrate the invention.:

Example 1:

5 Model studies were conducted on esters E-1 through E-6 to determine the possible rate enhancement which could be attained by using a dinucleophile rather than a mononucleophile to promote the removal from a phenolic moiety of a blocking group of this invention. Aqueous solutions A, B, and C, each containing 50% by volume of acetonitrile were prepared as follows (a separate solution A for each ester):

15 Solution A: 2.5×10^{-4} M ester (or 2.5×10^{-5} M E-1); 0.2N KCl
 Solution B: 25% by volume carbonate buffer (pH 10.0, ionic strength 0.75); 0.05N KCl
 Solution C: Solution B with added 0.05M hydroxylamine

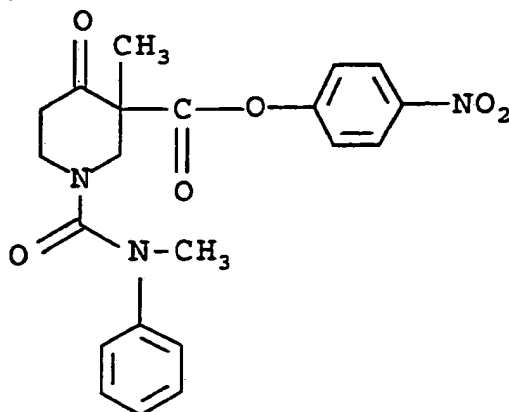
20 Then equal volumes of A and B (or A and C) were mixed at 25°C to give a pH 10.0 solution and the reaction was followed by spectrophotometric measurements of the phenol (290 nm) or p-
25 nitrophenol (402 nm) produced with time. In each case a reaction half-life ($t_{1/2}$) was calculated from the equation $t_{1/2} = \ln(2)/k$, where $\ln(2)$ is the natural logarithm of 2 and k is the pseudo first-order rate constant calculated for the
30 reaction. Smaller half-lives thus indicate more rapid reactions. The A+B combination provides an alkaline solution in which the main reactant is hydroxide ion (a mononucleophile) while in the A+C combination the active reactant is hydroxylamine (a
35 dinucleophile). A ratio of the A+B half-life to the A+C half-life provides a measure of rate

enhancement due to participation of hydroxylamine in the deblocking reaction. The results are shown in Table I:

TABLE I

5

E-1, INVENTION:



10

TABLE 1 E-2, INVENTION:

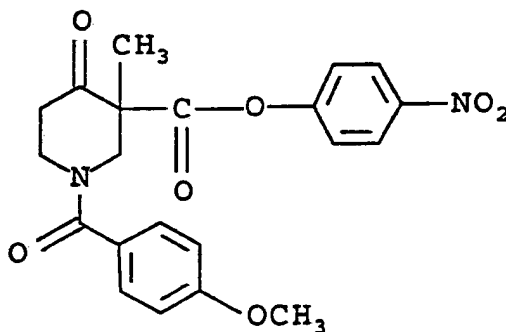
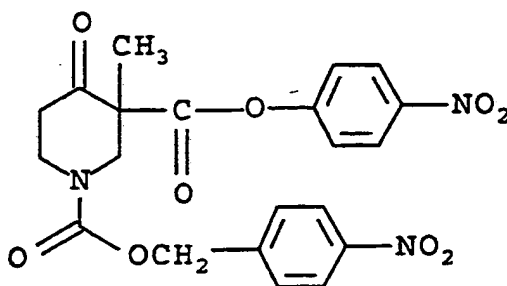


TABLE I E-3, INVENTION:



15

TABLE I...E-4, COMPARISON:

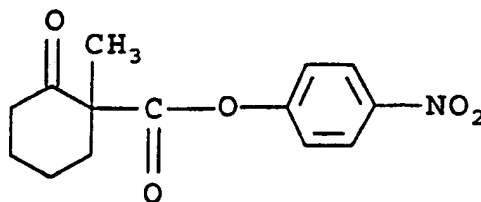


TABLE 1, E-5, COMPARISON:

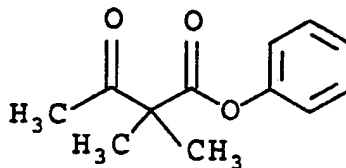
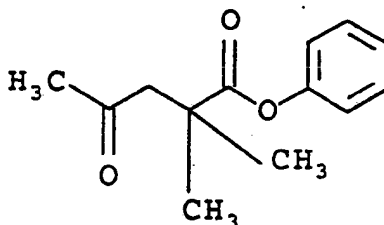


TABLE 1, E-6, COMPARISON:

TABLE I

Compound	$t_{1/2}^{A+B}$	$t_{1/2}^{A+C}$	Ratio
E-1 (Invention)	5.8×10^3	0.15	3.8×10^4
E-2 (Invention)	2.0×10^3	0.07	2.9×10^4
E-3 (Invention)	3.6×10^3	0.10	3.6×10^4
E-4 (Comparison)	2.5×10^5	1.10	2.3×10^5
E-5 (Comparison)	6.3×10^4	1.70	3.7×10^4
E-6 (Comparison)	1.3×10^5	790	1.7×10^2

Me herein means methyl.

It can be seen from Table I that esters E-1 and E-2 are much more reactive with the

dinucleophile hydroxylamine than are the comparisons. At the same time, the ratio of the two half-lives indicates that the compounds of the invention maintain excellent discrimination between reactions with a mononucleophile (hydroxide) and a
5 dinucleophile (hydroxylamine).

Example 2:

This example demonstrates that the use of a blocking group of the invention enables both hue
10 shifting and quantitative release during processing of a masking coupler within a photographic element. A red sensitized silver bromiodide gelatin emulsion (0.75 micron diameter, 0.13 micron thick) was mixed with a coupler dispersion comprising cyan
15 coupler C-1 dispersed in half its weight of di-n-butyl phthalate and a masking coupler dispersed in twice its weight of either di-n-butyl phthalate (CS-1) or 2,4-di-tertamyphenol (CS-2). Note that the masking couplers MC-1 and MC-2 are blocked
20 versions of the masking coupler MC-3. The resulting mixture was coated on a photographic film support according to the following format (amounts of each component are given in mg/m^2 with silver halide counted as silver).

25

Overcoat	gelatin (2691);
Layer	bis(vinylsulfonyl-methyl) ether hardener (1.75% of total gelatin weight)

30

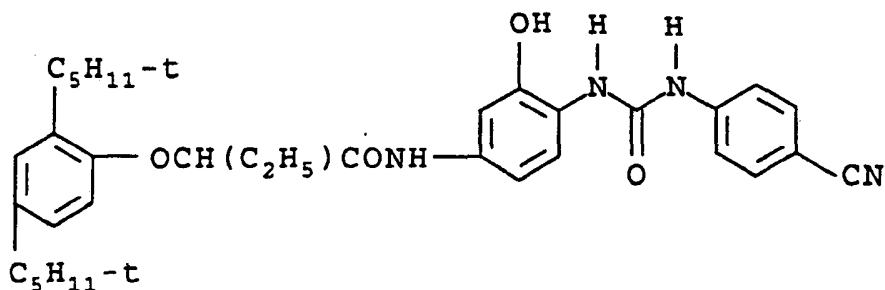
Emulsion	gelatin (3767); red-sensitized
Layer:	AgBrI emulsion (1076); cyan coupler C-1 (774); and a blocked masking coupler ($215\text{mmol}/\text{m}^2$)

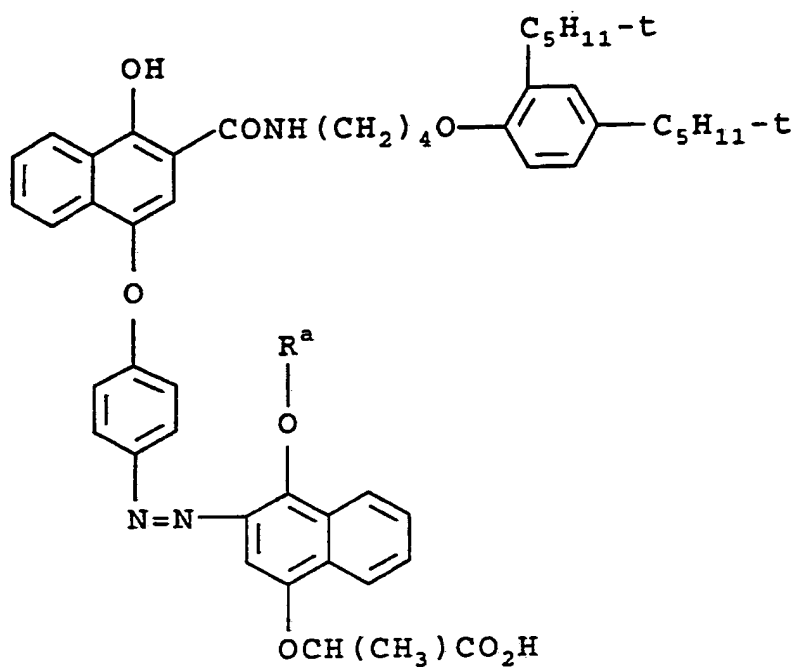
35

Film Support: gelatin (4887) on 132 micron
cellulose acetate with remjet
backing

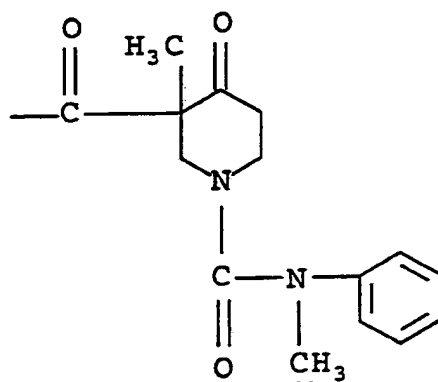
Each photographic element was imagewise
exposed to light through a graduated density test
object in a commercial sensitometer to provide a
developable latent image (5500°K light source, 0-4
step wedge, with Wratten 99 plus 0.1 ND filter.
Wratten is a trademark of Eastman Kodak Co.,
U.S.A.). The resulting photographic film was then
developed and processed in a commercial C-41
process of the Eastman Kodak Co. U.S.A. without the
final stabilizer step. This process and the
processing compositions for the process are
described in, for example, British Journal of
Photography Annual, 1988, pages 191-199. The
development process was carried out with and
without hydroxylamine sulfate (HAS) in the color
developer solution. Densitometric measurements
made with green light are shown in Table II.

Cyan Coupler C-1

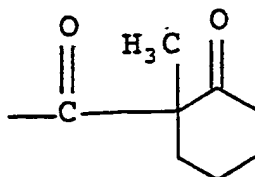


Masking Couplers

5 MC-1 (Invention), R^a=:



MC-2 (Comparison), R^a=:



10

MC-3 (Comparison), R^a= H

"D_g at E_{min}" is the green density at minimum exposure. This indicates the ability of the blocking group to shift the visible absorption of the masking dye and the extent to which the blocking group has been removed from (and masking chromophore regenerated in) the blocked masking couplers MC-1 and MC-2. Higher values correspond to greater extents of deblocking. Hence, higher values are desirable for the hydroxylamine-containing process, lower values are desirable for the process without hydroxylamine. "WD_g" is the difference between (D_g at E_{min}) values for the two developers. HAS herein is hydroxylamine sulfate.

TABLE II

	(Invention)		(Comparison)		(Comparison)	
	<u>MC-1</u>		<u>MC-2</u>		<u>MC-3</u>	
	<u>CS-1</u>	<u>CS-2</u>	<u>CS-1</u>	<u>CS-2</u>	<u>CS-1</u>	<u>CS-2</u>
D _g at E _{min} (with HAS)	0.32	0.35	0.20	0.19	0.35	0.31
D _g at E _{min} (w/o HAS)	0.09	0.09	0.09	0.09	0.33	0.30
WD _g	0.23	0.26	0.11	0.10	0.02	0.01

These data demonstrate that both MC-1 and MC-2 are successful at shifting the hue of the masking coupler so as to minimize green absorption prior to deblocking. However, MC-1 was quantitatively deblocked during the hydroxylamine process, but MC-2 was only partially deblocked. Thus, only the compound of the invention, MC-1, exhibited excellent hue shifting prior to deblocking and quantitative deblocking on

processing.

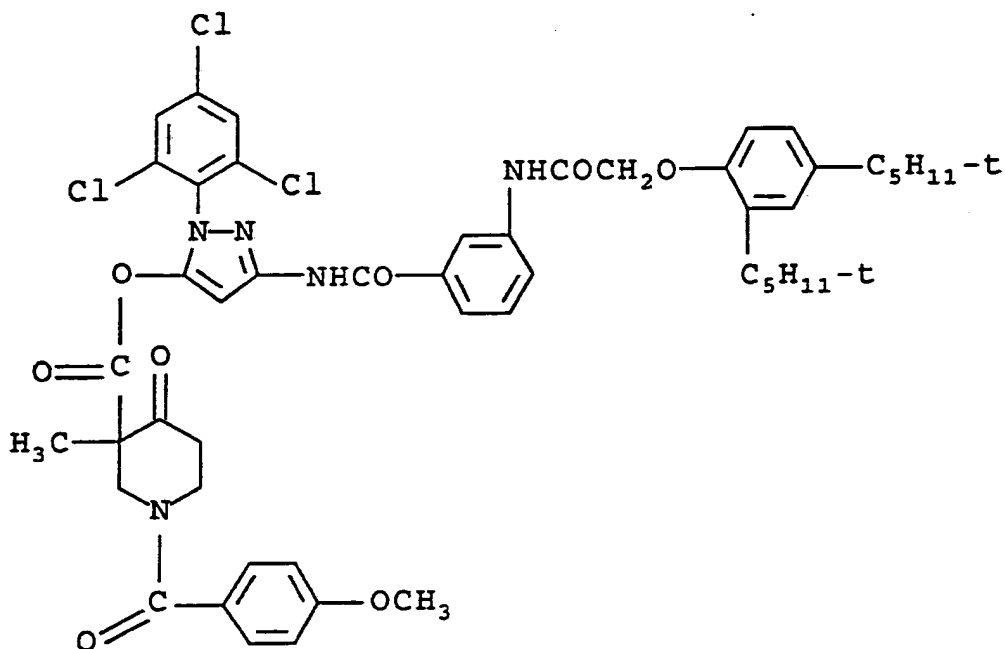
Examples 3 - 64:

5 The following blocked photographically
useful compounds can be prepared by the methods
described. These blocked compounds can be
incorporated and processed in a photographic
element as described, such as in the element and
process of Example 1: (The example number is given
for each compound.)

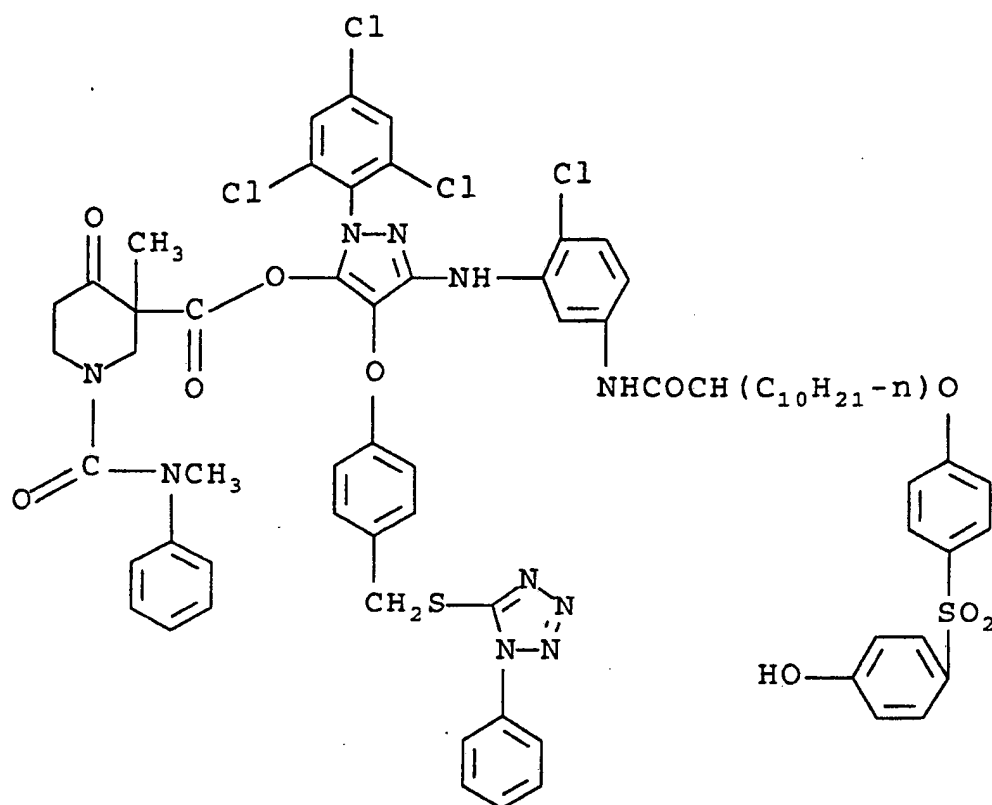
10

IMAGE COUPLERS:

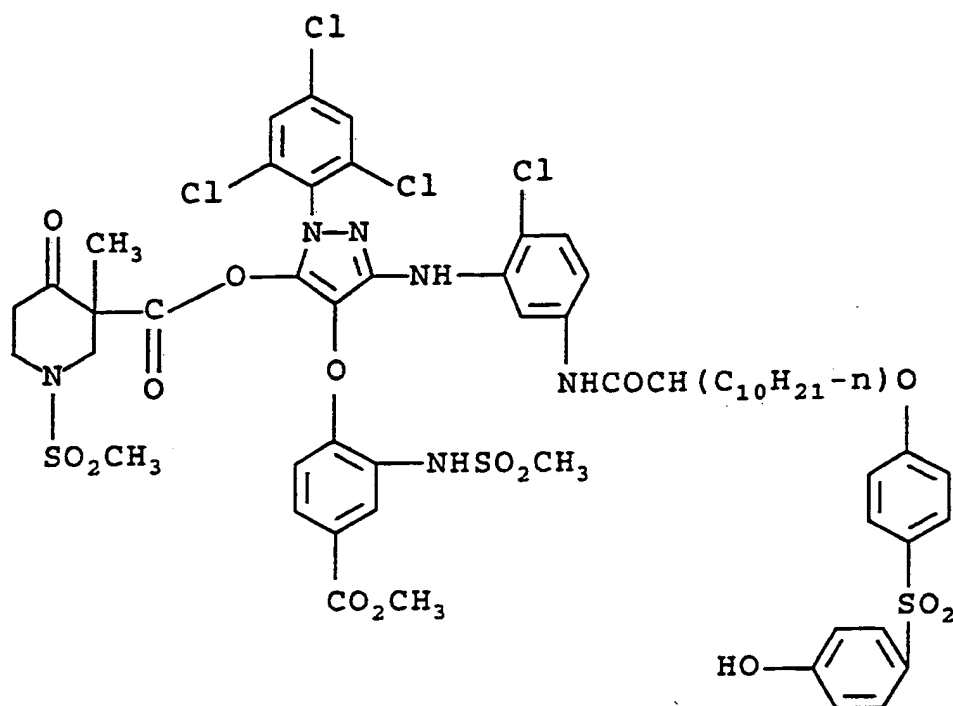
3.



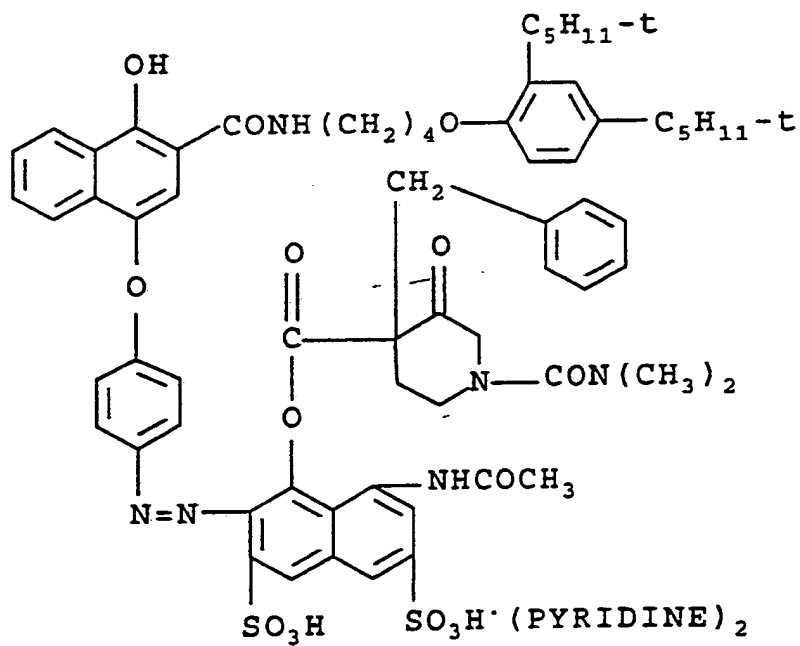
4:



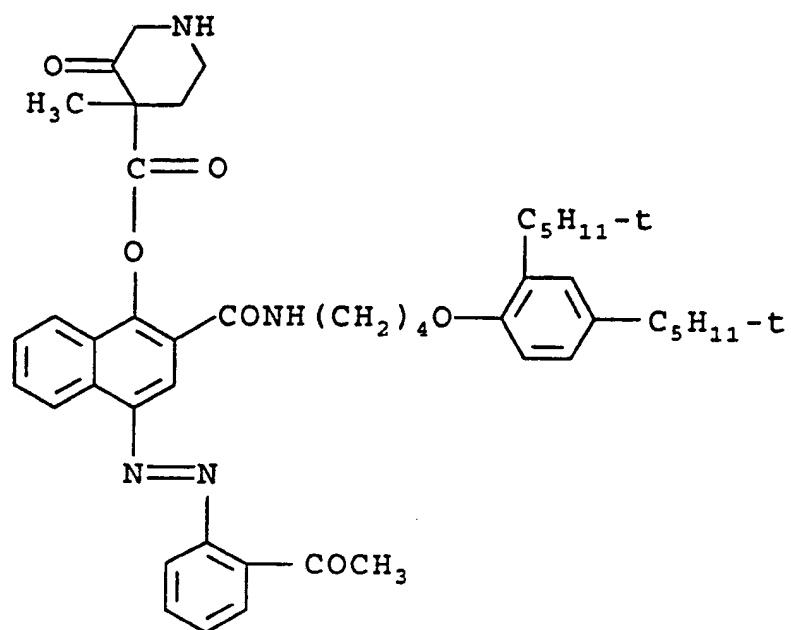
5.

5 MASKING COUPLERS:

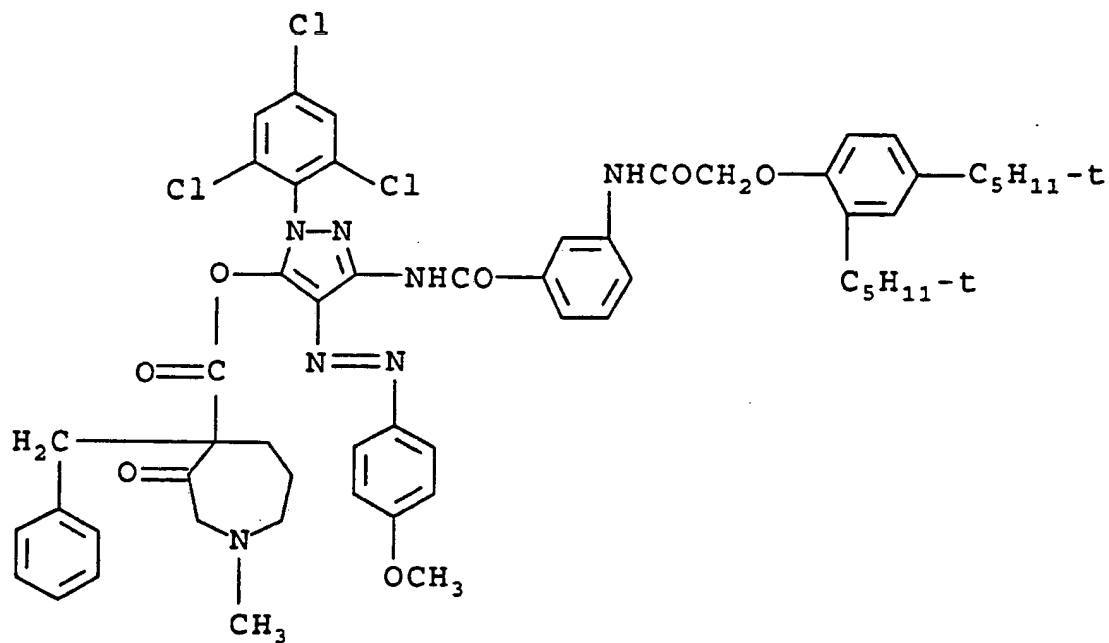
6.



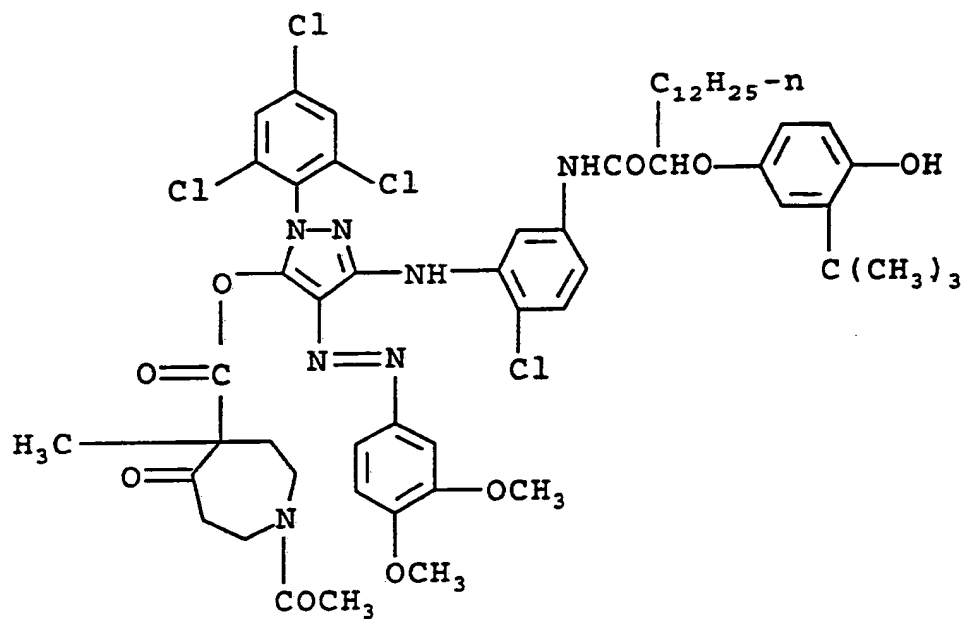
7.



5 8.

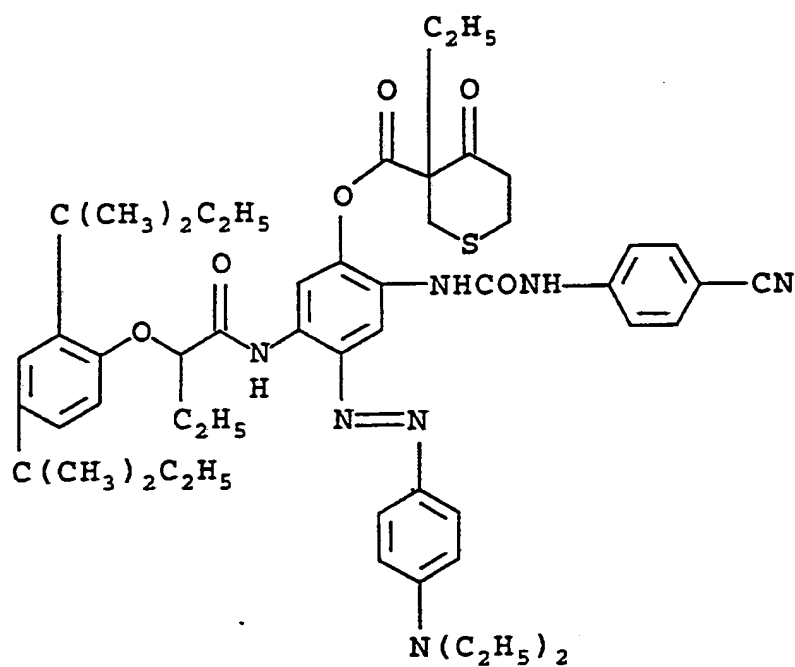


9.

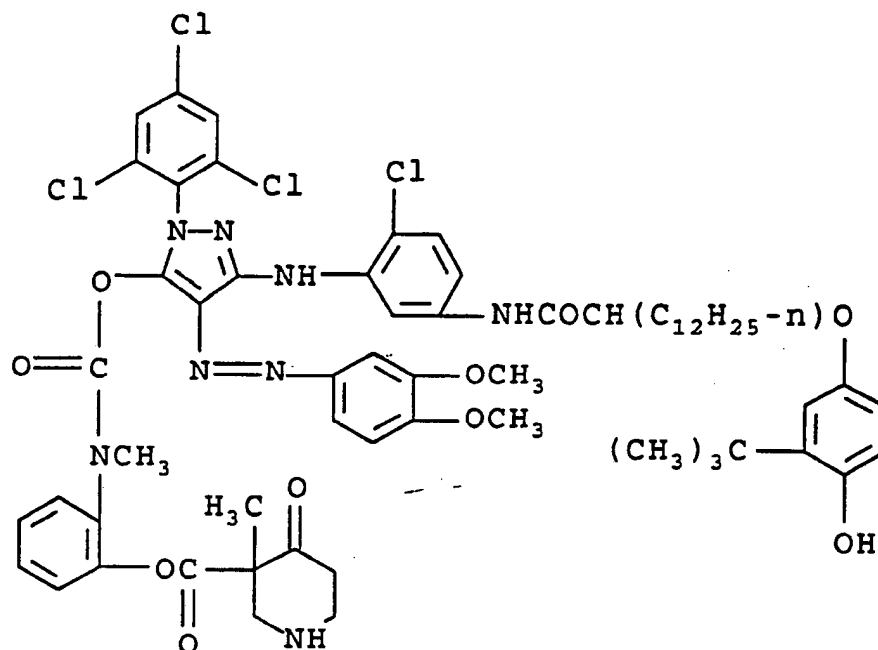


10.

5



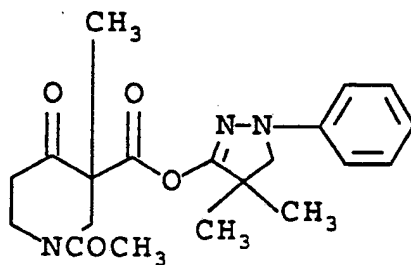
11.



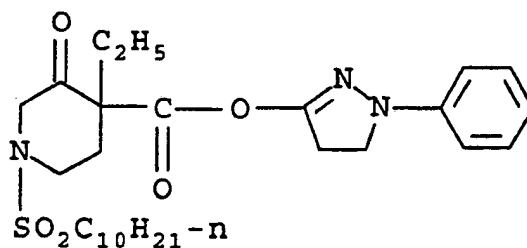
Development Accelerators and Electron Transfer Agents

5

12.

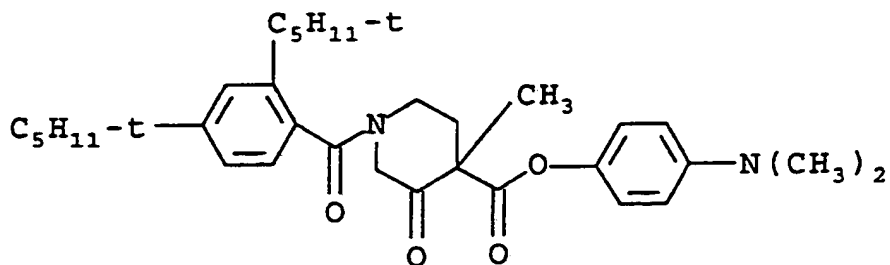


13.

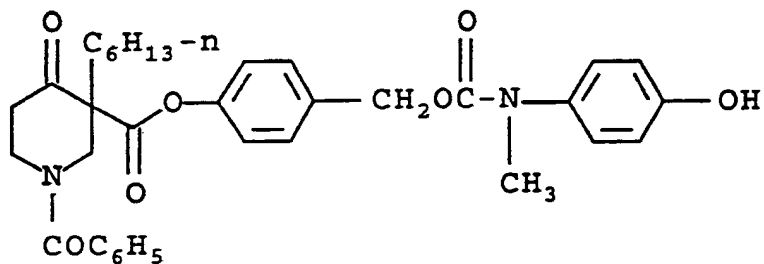


10

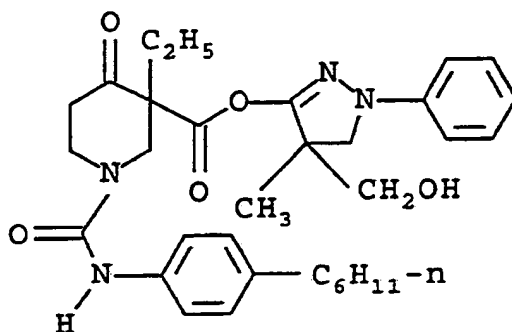
14.



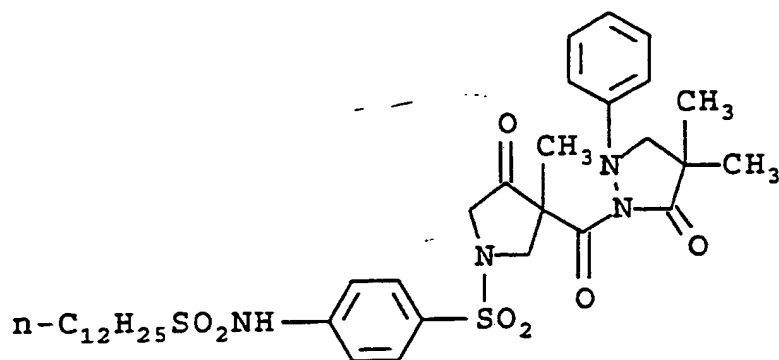
15.



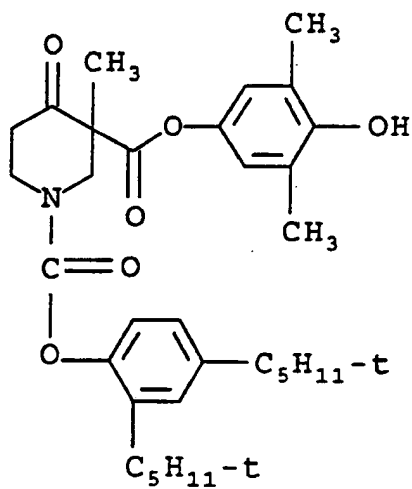
5 16:



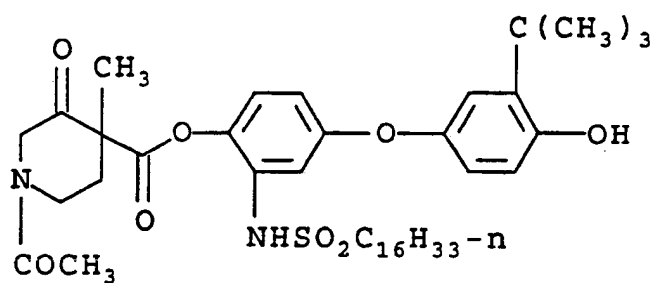
17:



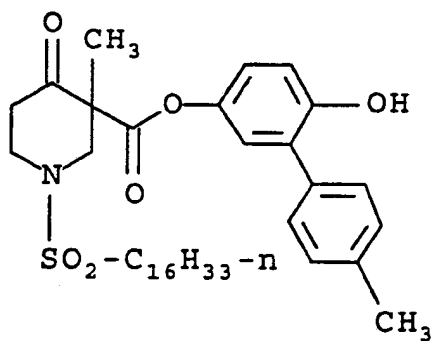
18:



19:

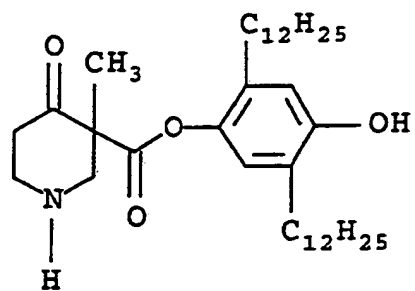


5 20:

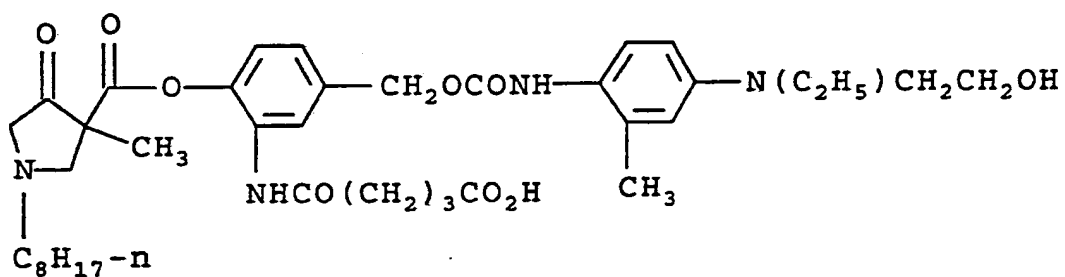


Dox Scavenger:

21:

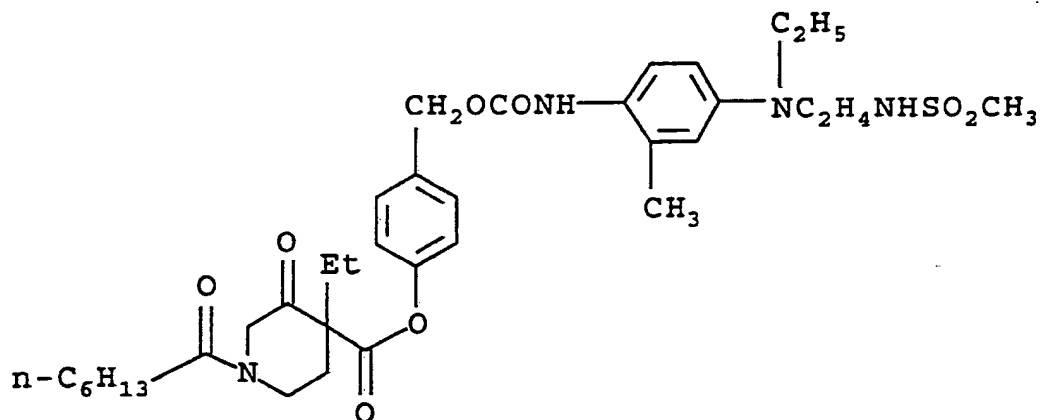
5 Color Developer:

22:



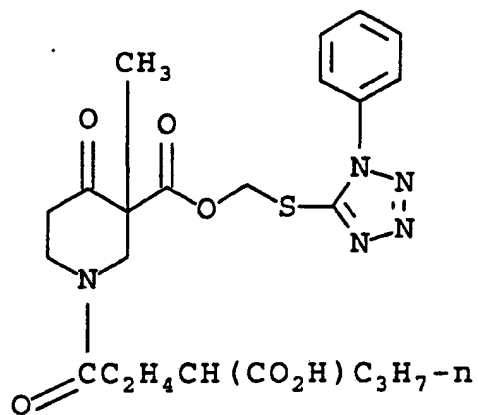
10

23:

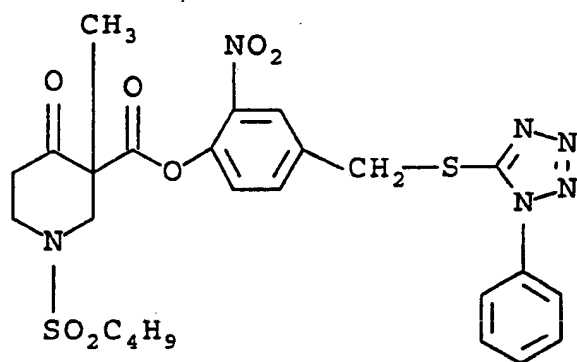


15

24:



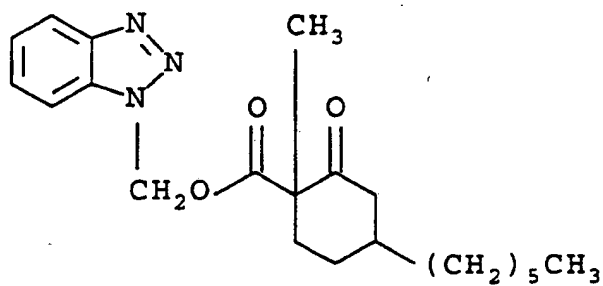
25:



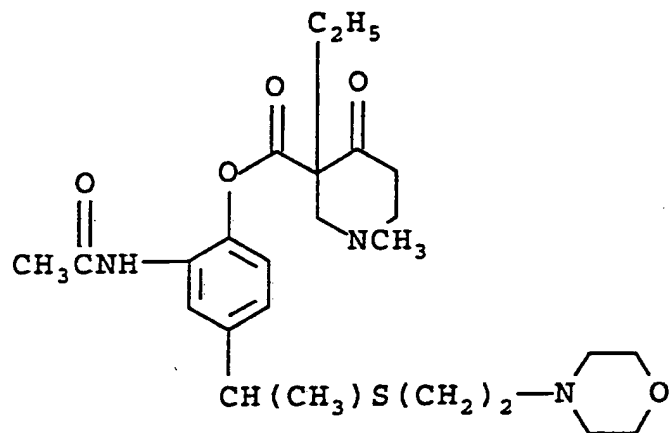
5

Compounds having the foregoing or other functions:

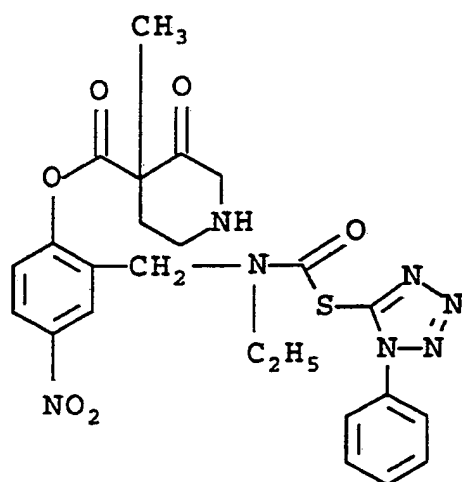
10. COMPOUND 26:



COMPOUND 27:

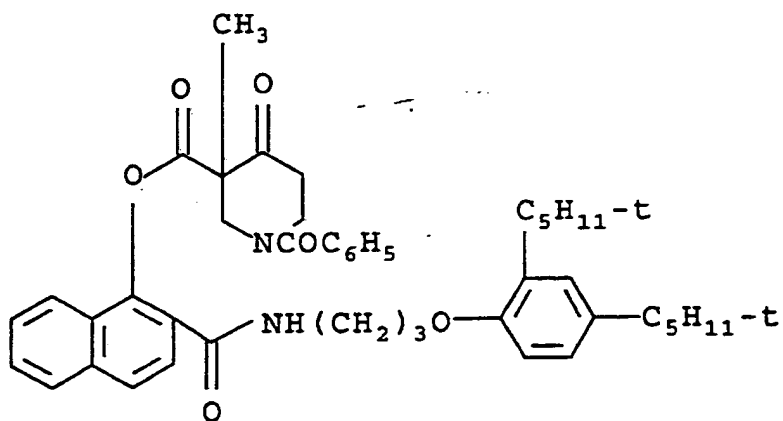


COMPOUND 28:



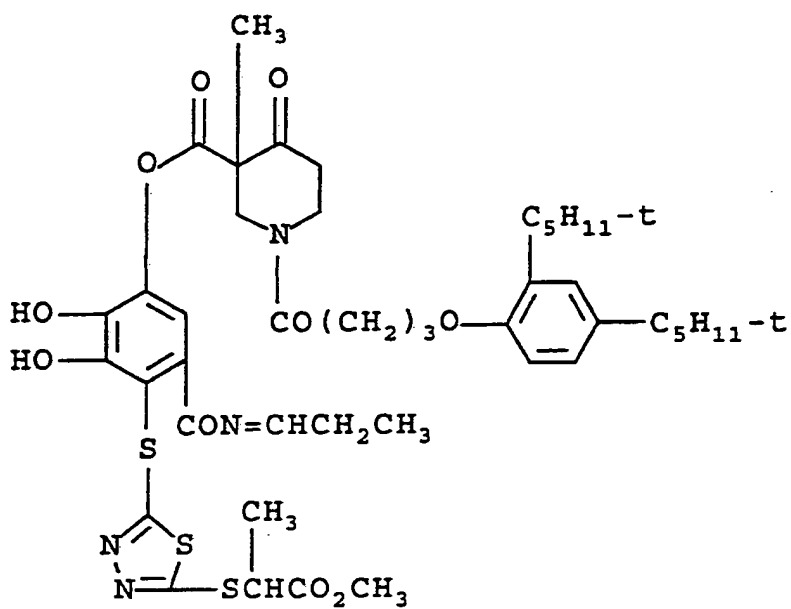
5

COMPOUND 29:

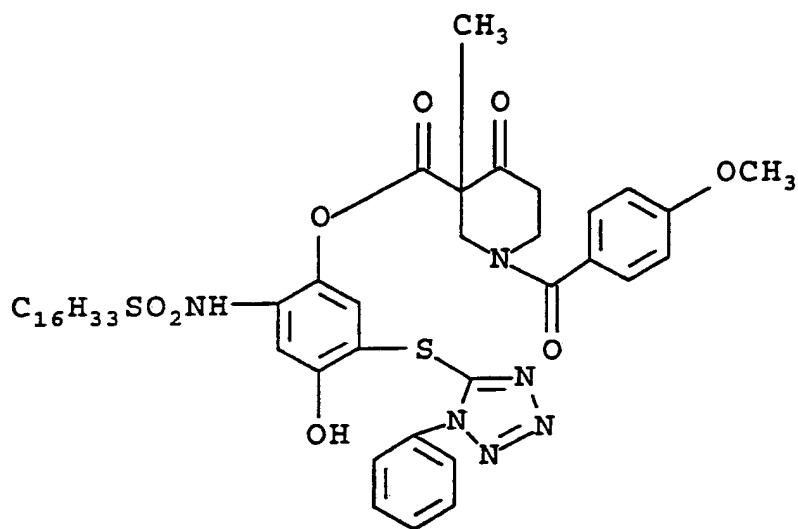


CCS(=O)(=O)N1CCCCC1C(=O)C(C)C(=O)Oc2ccc3cc(OCc4ccccc4=N=Nc5cc(OC(=O)N)ccc5S(=O)(=O)[O-])ccc3c2Oc6ccc(cc6)C7H15CCCCCCCCCCCCCCCCNC(=O)c1ccc(OC(=O)C2CCN(C2)C(=O)CC3=CC=CC=C3)cc1OCCSCC(=O)O

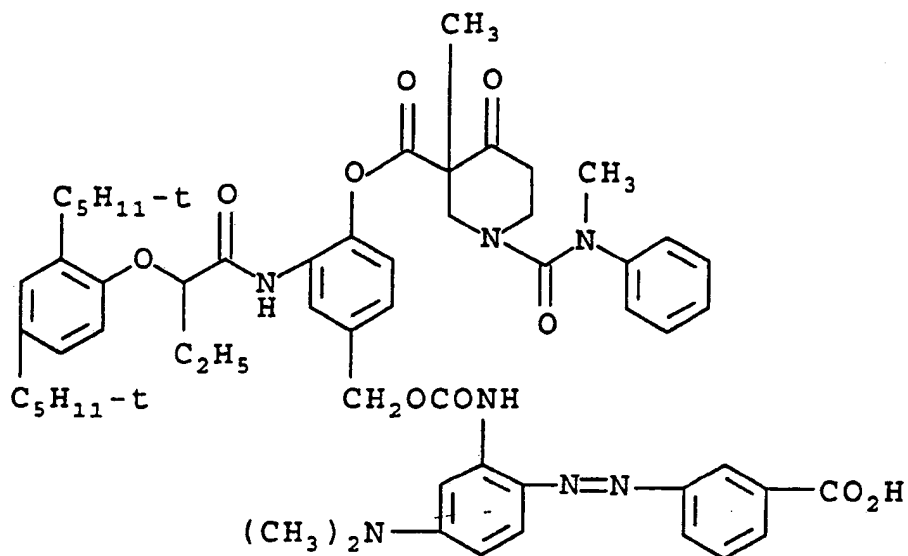
COMPOUND 32:



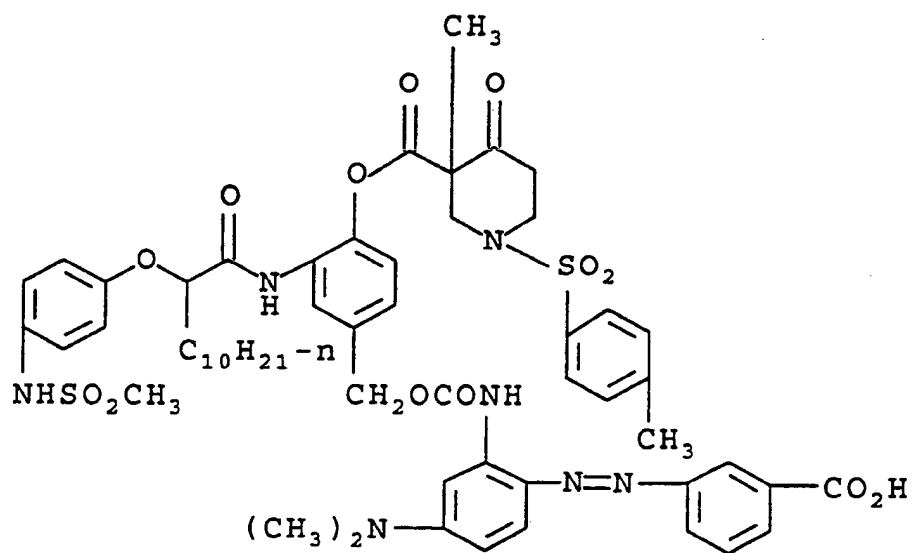
COMPOUND 33:



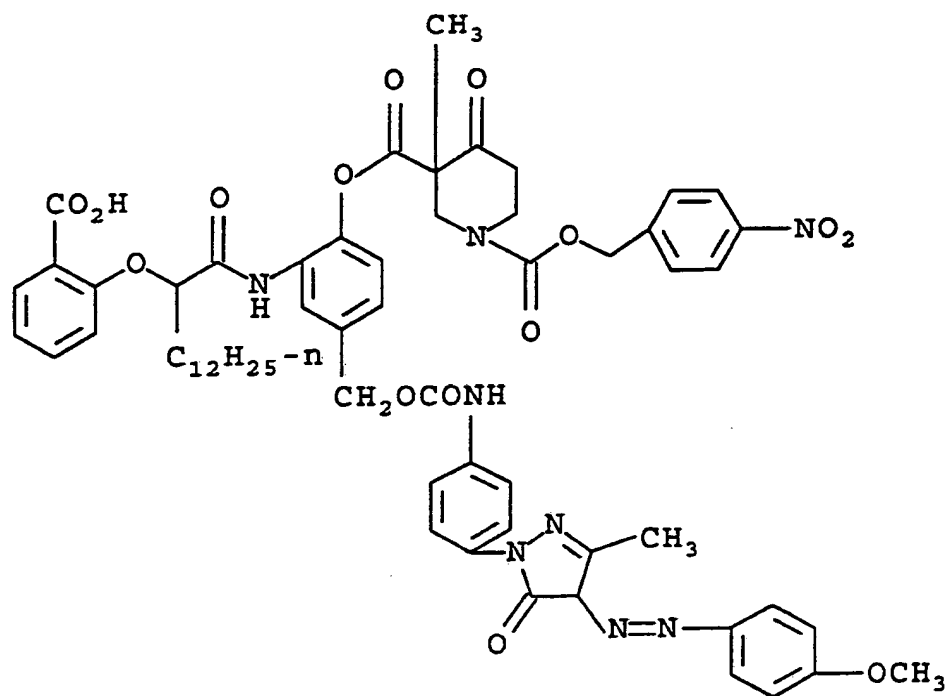
COMPOUND 34:



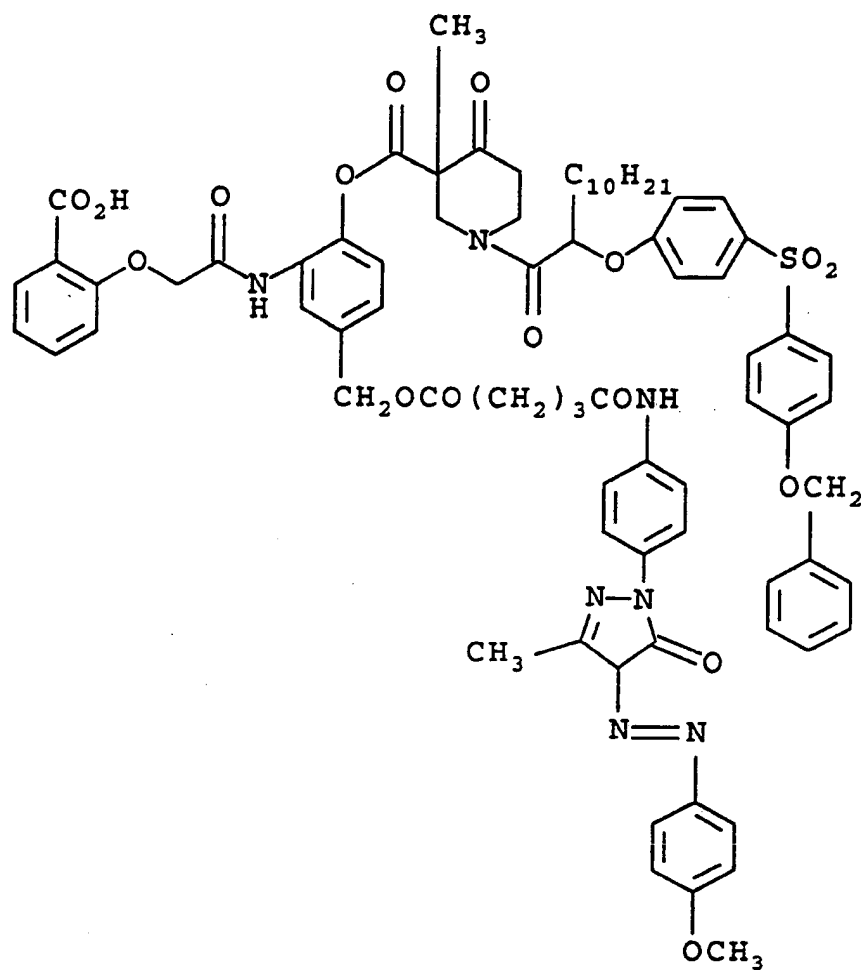
5 COMPOUND 35:



COMPOUND 36:

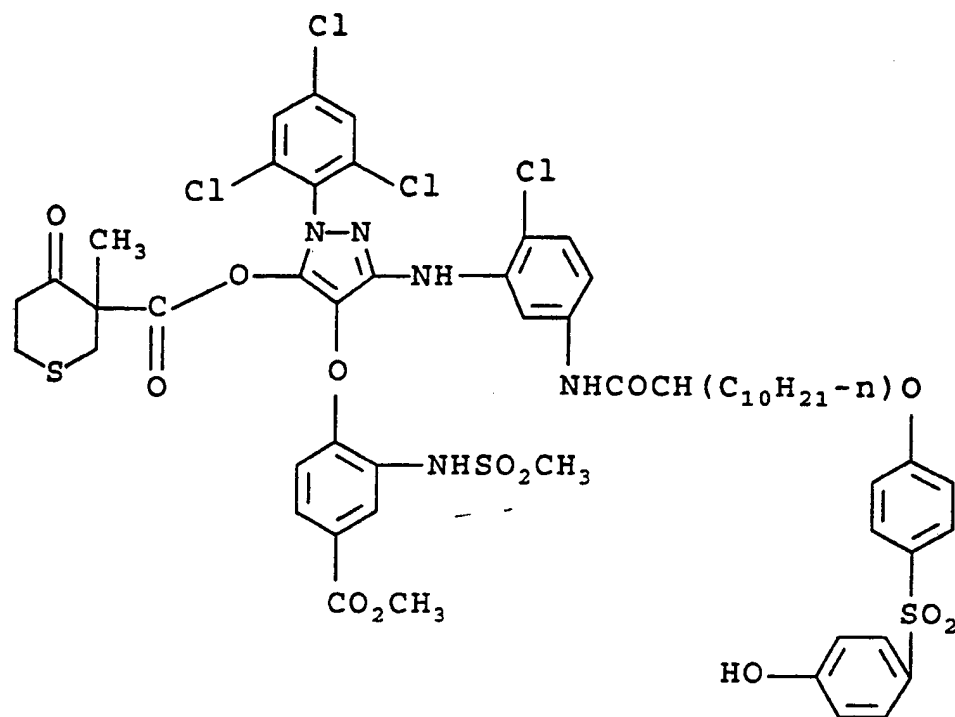


COMPOUND 37

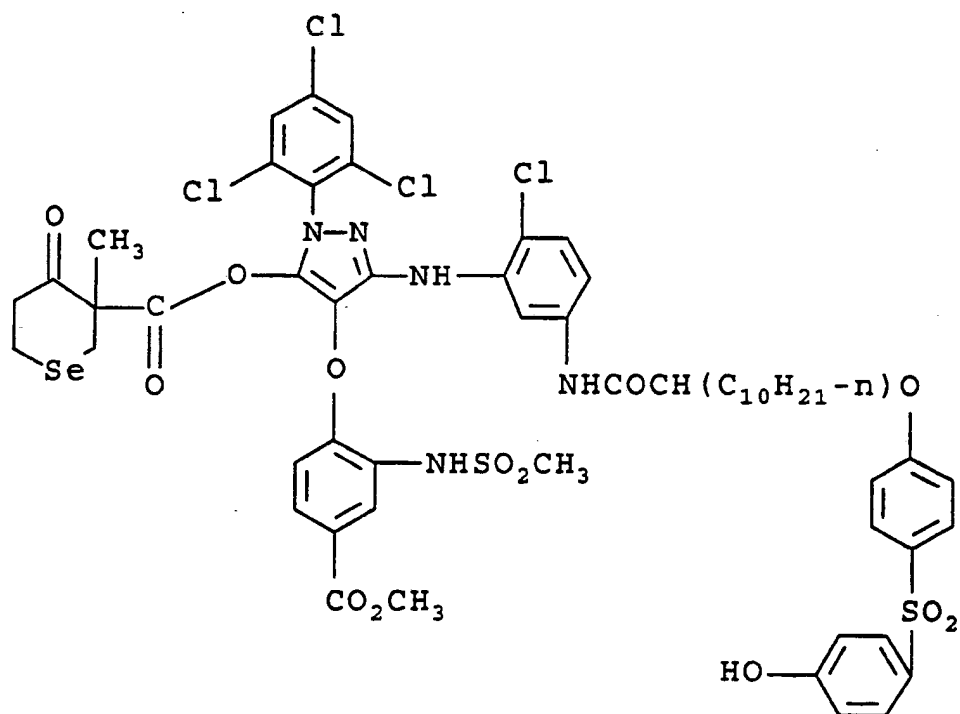


CCCCCc1ccc(OC(=O)Nc2c(O)c3ccccc3cc2Oc4ccc(cc4)/N=N/c5ccc6c(c5)OC(=O)C)cc1CCCCC1C(=O)N(C)Cc7ccccc7CCCCCc1ccc(OCCCCC(=O)N2CCCCC2C(=O)C(=O)SCCCN3CCOCC3)cc1CCCCC

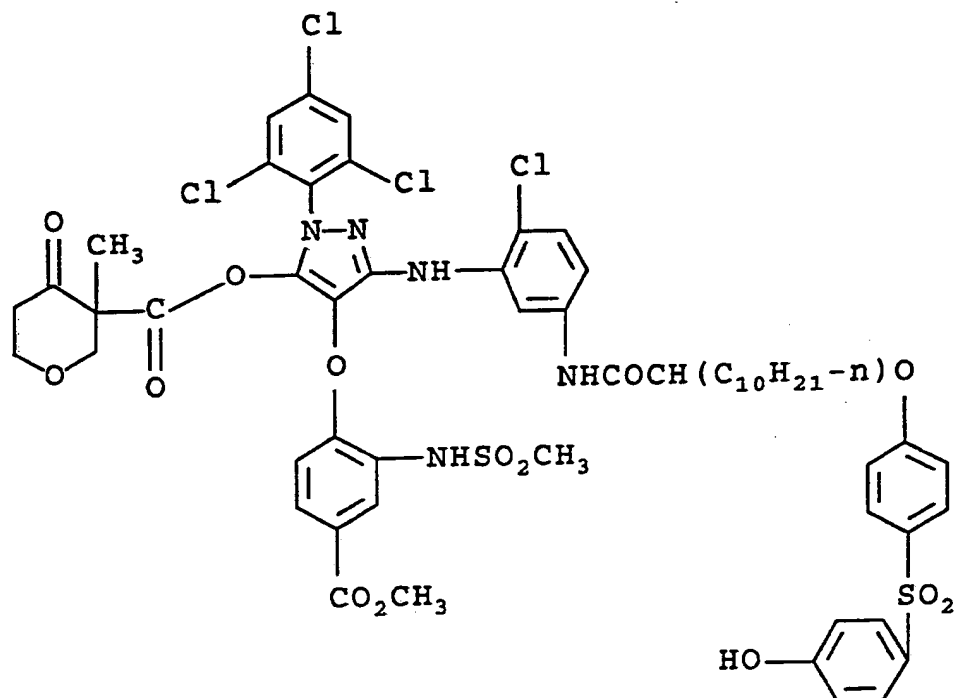
40.



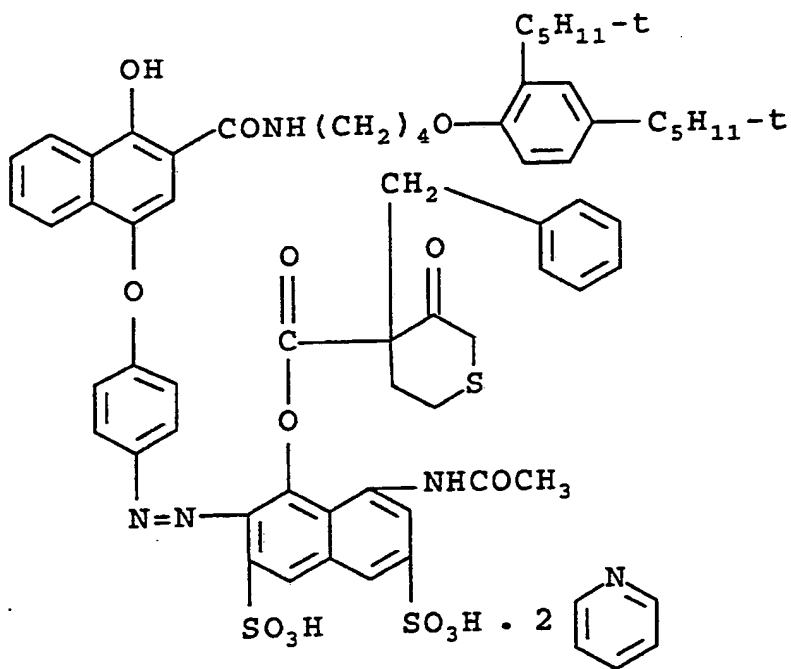
41.



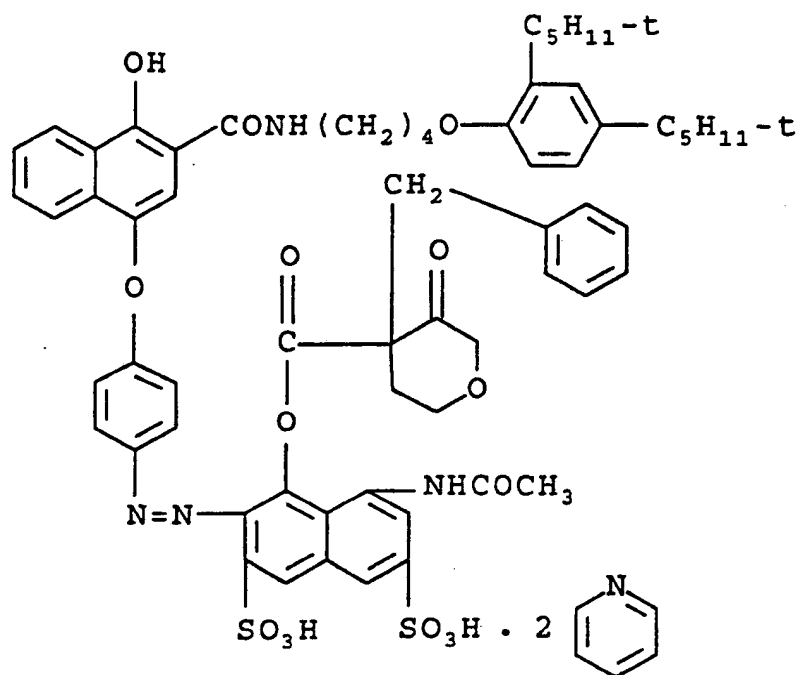
42.



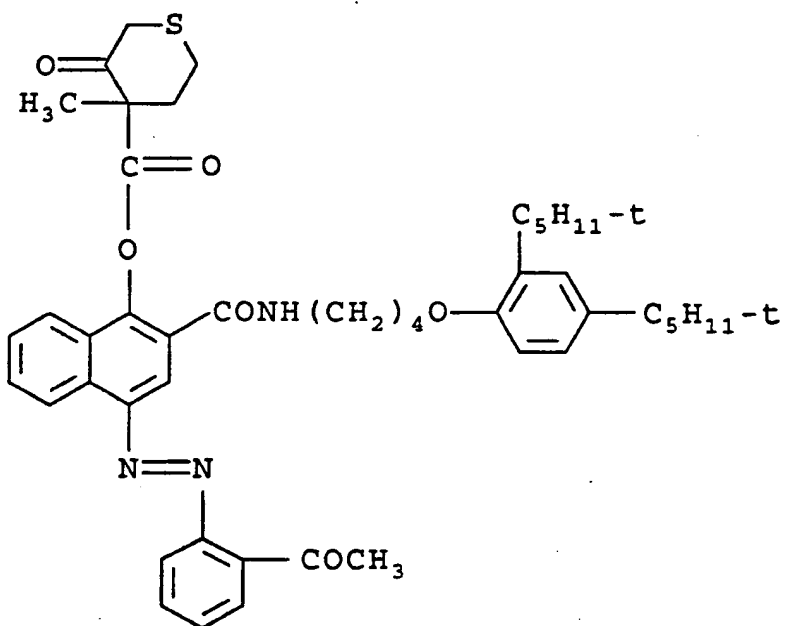
43:



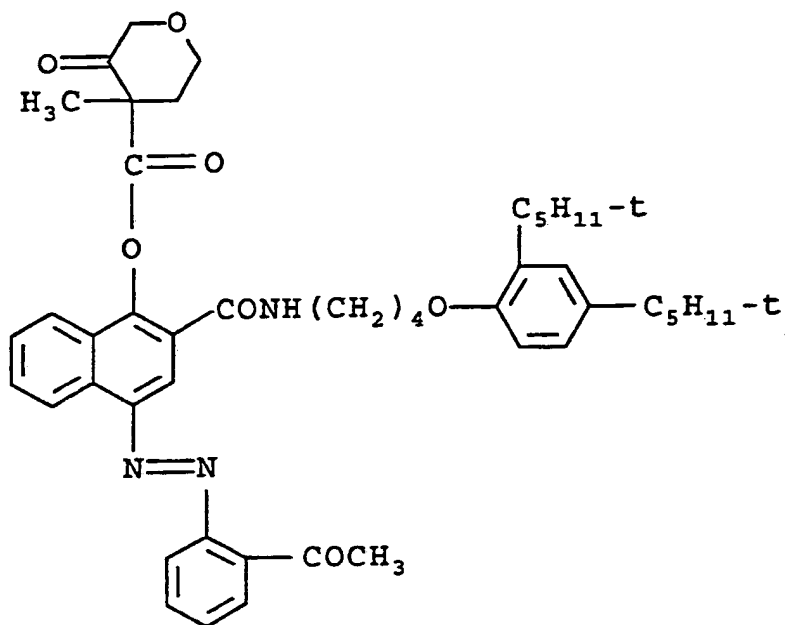
44.



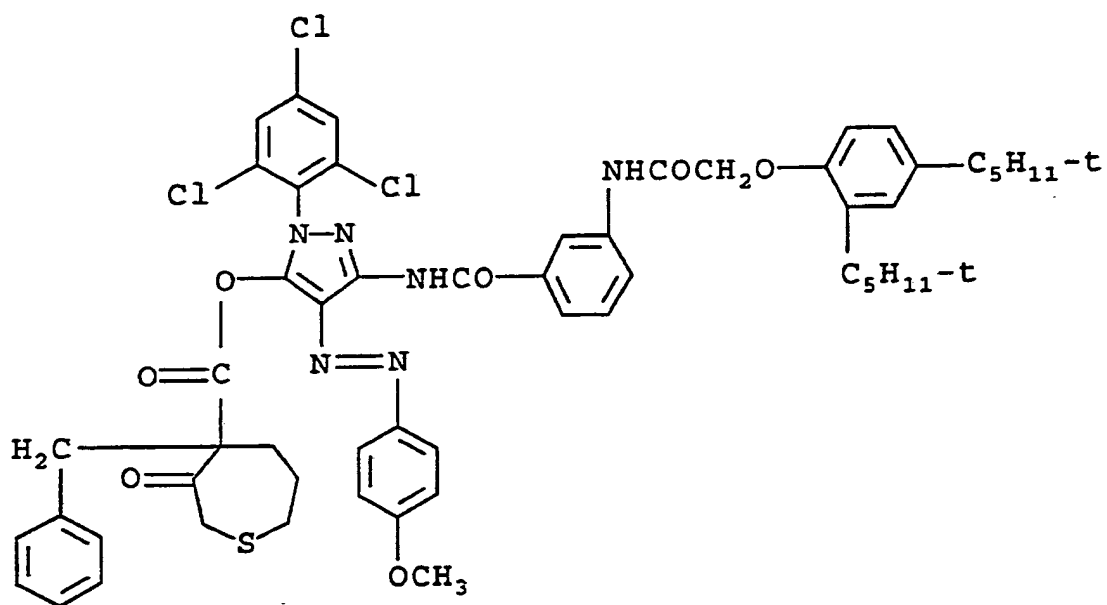
45:



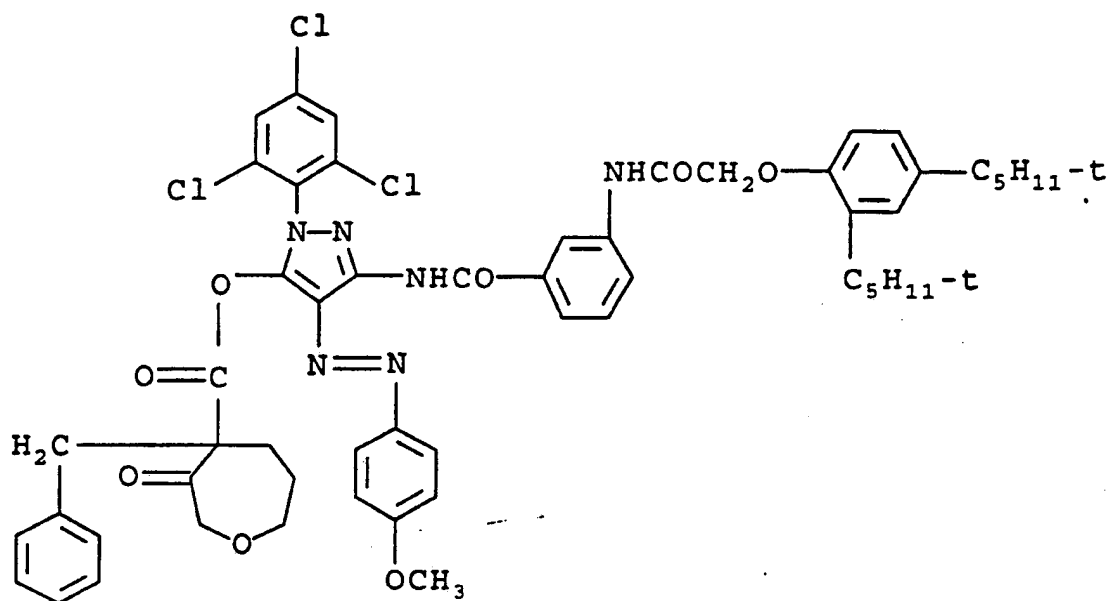
46:



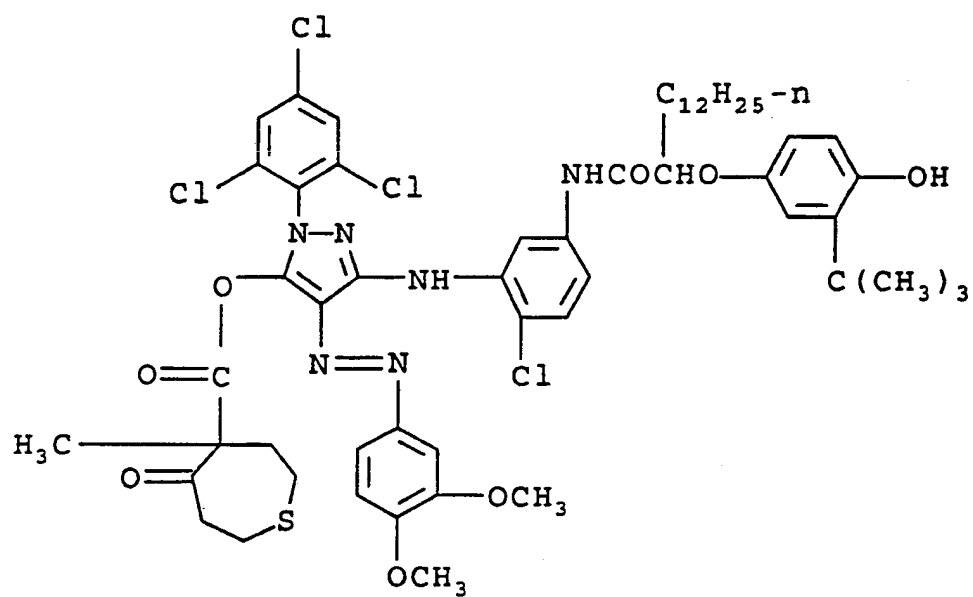
47:



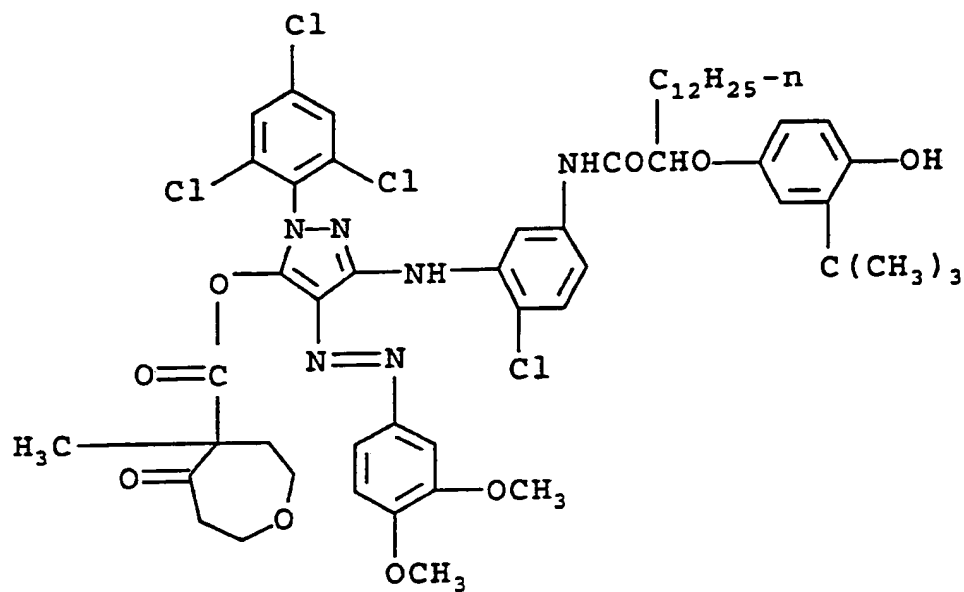
48:



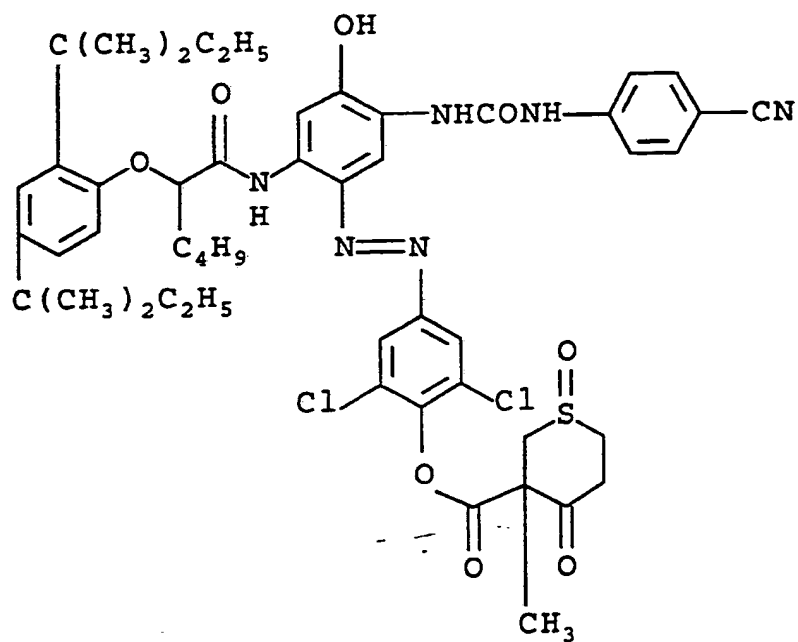
49:



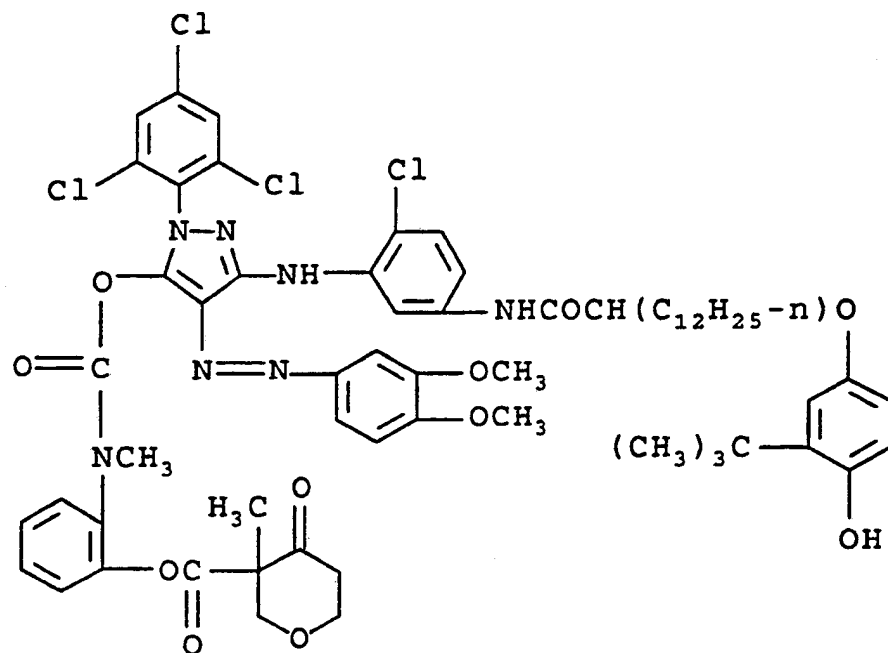
50:



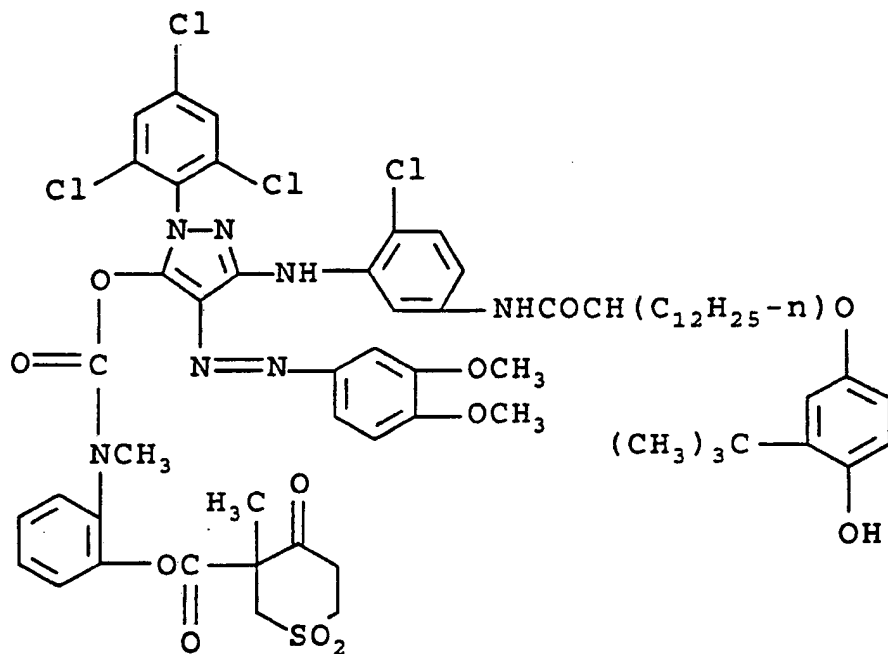
51:



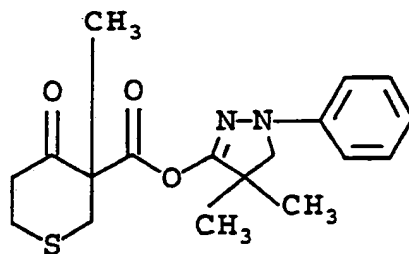
52:



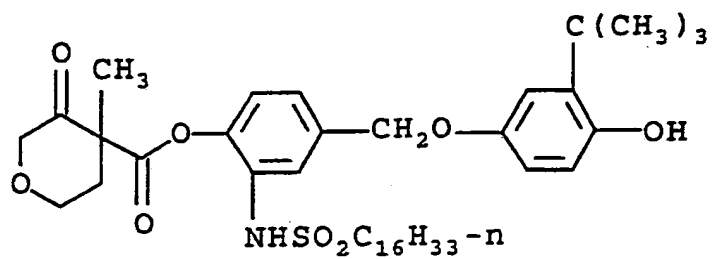
5 53:



54:

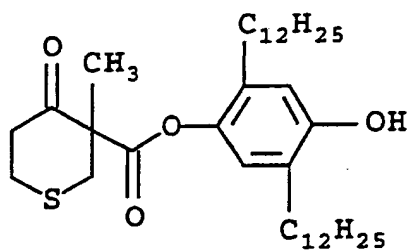


55:

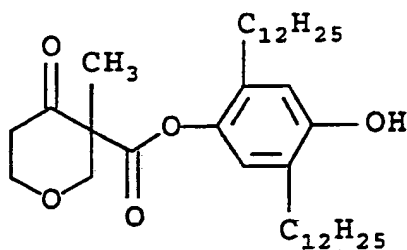


5

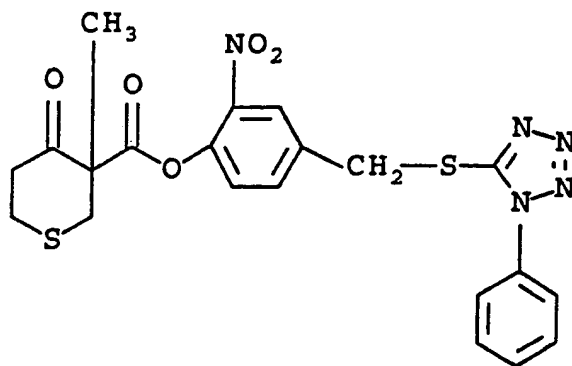
56:



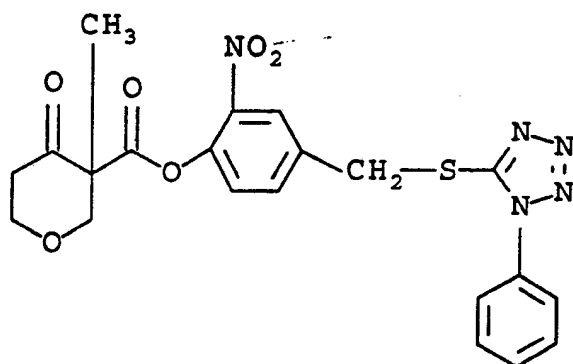
10 COMPOUND 57:



COMPOUND 58:

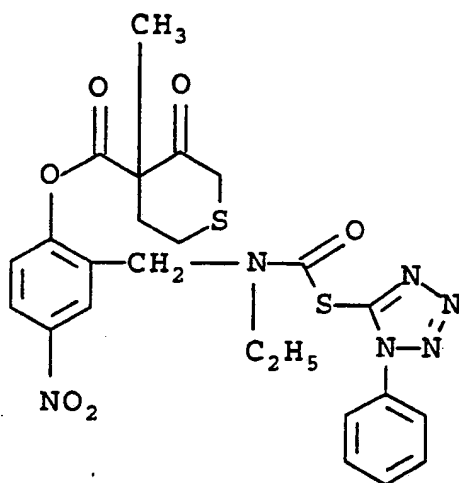


COMPOUND 59:

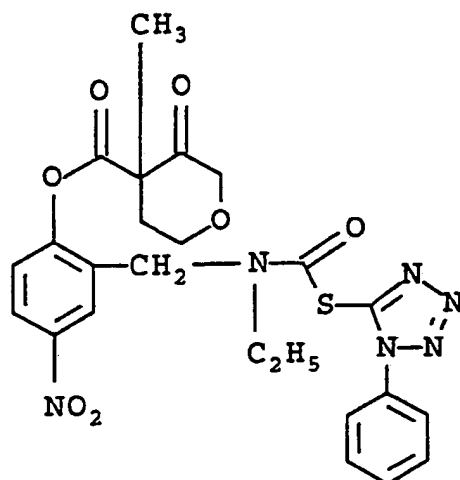


5

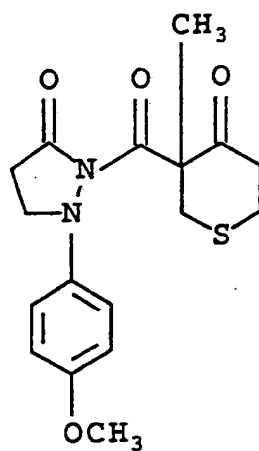
COMPOUND 60:



COMPOUND 61:

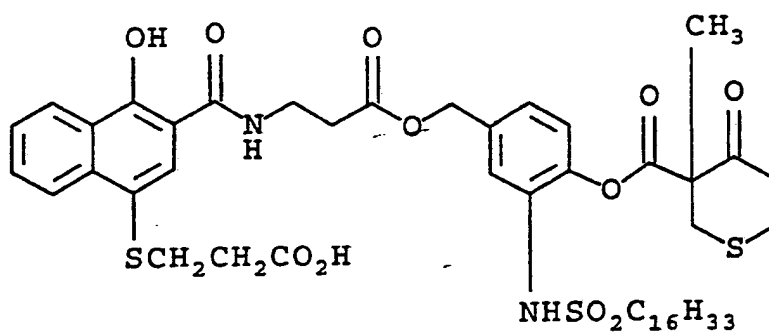


COMPOUND 62:

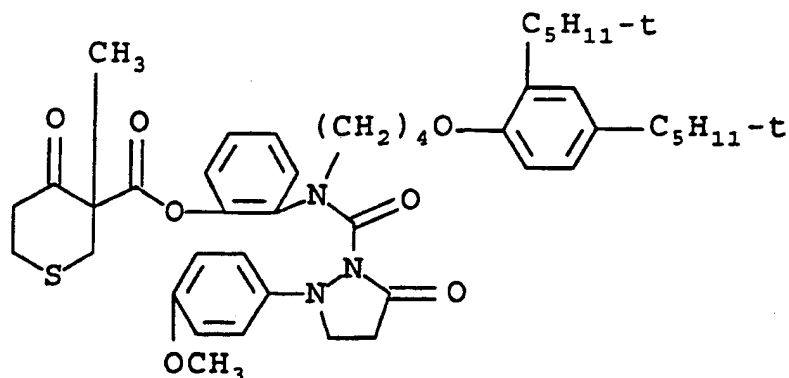


5

COMPOUND 63:

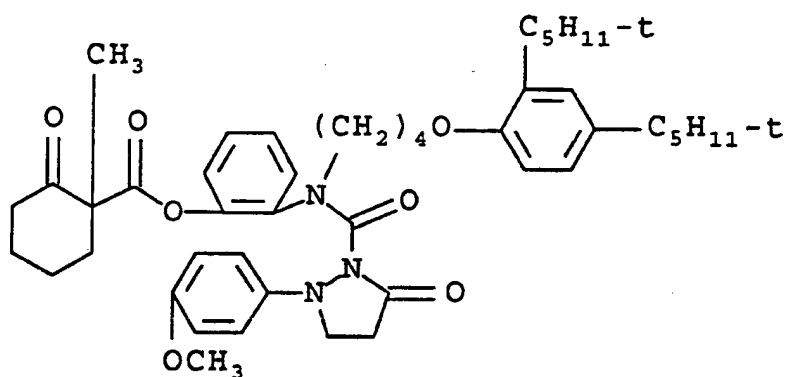


COMPOUND 64:



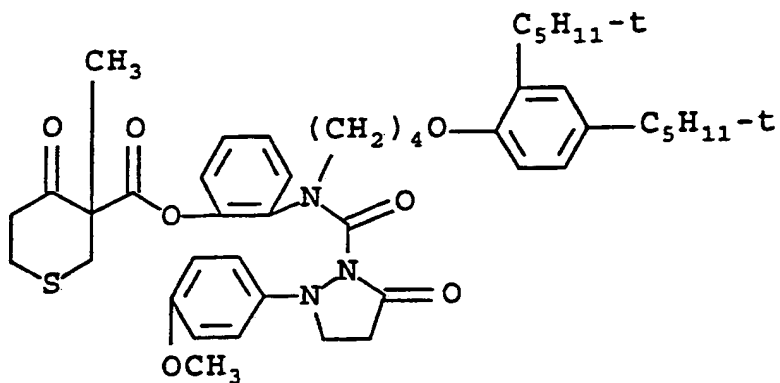
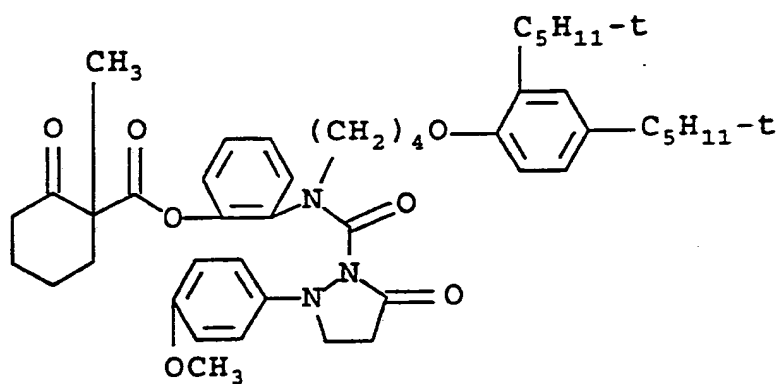
COMPARISON COMPOUND:

5

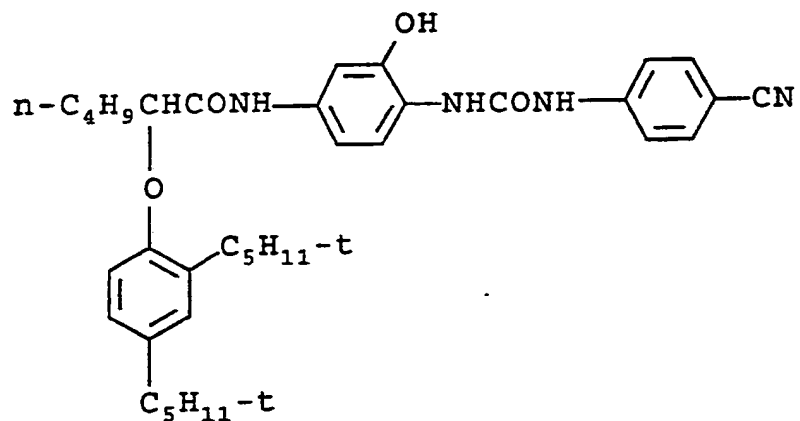
Example 65

10 This example demonstrates that the use of a blocking group containing a sulfur atom in accordance with the invention provides a quicker release of the electron transfer agent, as measured by the resulting contrast, speed, and maximum density compared to the identical material without the sulfur atom.

15

Invention:Comparison:

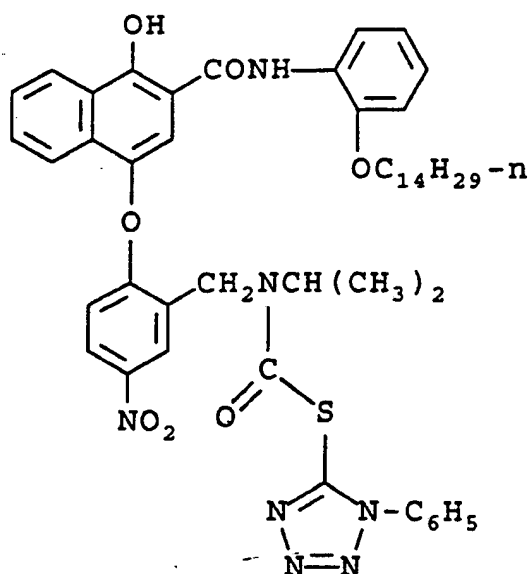
5

Image Coupler

1):

DIAR Coupler (C-2):

10



Evaluation Format:

- The compounds were dispersed using diethyl
- 5 lauramide (2 parts by weight) and ethyl acetate (3 parts by weight) to prepare a dispersion that was 1% compound (w/w) and 6% gelatin (w/w). A fine particle size dispersion was obtained using a colloid mill, as is well known in the art. The dispersions were used unwashed and
 - 10 included in the emulsion containing a layer of the monochrome test format described below. Other constituents of this layer were gelatin, water, saponin, a red sensitized silver bromiodide emulsion (3 mole % iodide, tabular grain, 0.75 μm average diameter, 0.13 μm
 - 15 average thickness), an image coupler (C-1) and development inhibitor anchimeric releasing (DIAR) coupler (C-2). Above this was coated a protective overcoat.

20

(OVERCOAT LAYER)

Gelatin (5.38 g/m^2)

1,1'-[Oxybis(methylene sulphonyl)]bis-ethene (2% of total gelatin) hardener;

Saponin (1.5% melt volume)

(EMULSION LAYER)

- 5 Gelatin (2.69% g/m²);
Saponin (1.5% melt volume);
Emulsion (1.61 g Ag/m²);
Couplers C-1 (0.54 g/m²), C-2 (0.04 g/m²);
+/- electron transfer compound (161 or 269 μ mole/m²)

- 10 Samples of these monochrome coatings were
imagewise exposed through a graduated density test object
and processed at 100 degrees F. using a KODAK C41
protocol modified to include a stop bath (30 sec.).
Sensitometric data are shown below:

15

<u>COATING</u>	<u>ETA</u> <u>RELEASER</u> <u>μMOLE/M²</u>	<u>CONTRAST</u>	<u>SPEED</u>	<u>D_{MAX}</u>
Invention	161	0.595	215	.930
Invention	269	0.467	223	.807
Comparison	161	0.465	211	.821
Comparison	269	0.358	211	.597

This compares the non-imagewise release of ETA from the invention and the comparison without sulfur with the invention results clearly superior.

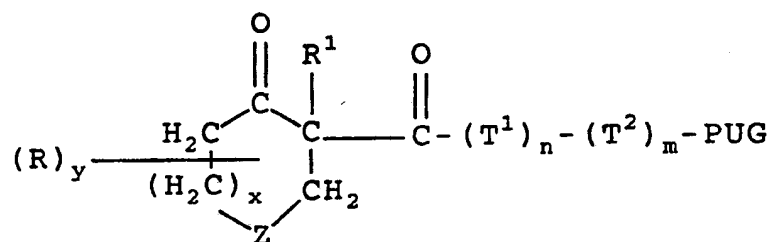
- 20 The invention has been described in detail
with particular reference to particular embodiments
thereof, but it will be understood that variations
and modifications can be effected within the spirit
and scope of the invention.

WHAT IS CLAIMED IS:

1. A photographic element comprising a support bearing at least one silver halide photographic emulsion layer and a blocked photographically useful compound comprising a photographically useful group and a blocking group that is capable of releasing the photographically useful group upon processing the photographic element, wherein the blocking group comprises a beta-ketocarbonyl group that is part of a 5 to 7 member heterocyclic ring containing a heteroatom selected from the group consisting of nitrogen, sulfur, selenium and oxygen located at a position not adjacent to the beta-ketocarbonyl group.

2. A photographic element as in Claim 1 wherein the blocked photographically useful compound is represented by the formula:

15 2. A photographic element as in Claim 1
wherein the blocked photographically useful
compound is represented by the formula:



20 wherein

T¹ and T² individually are releasable timing groups;

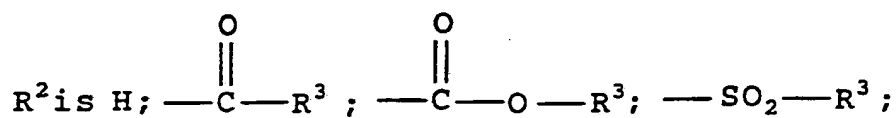
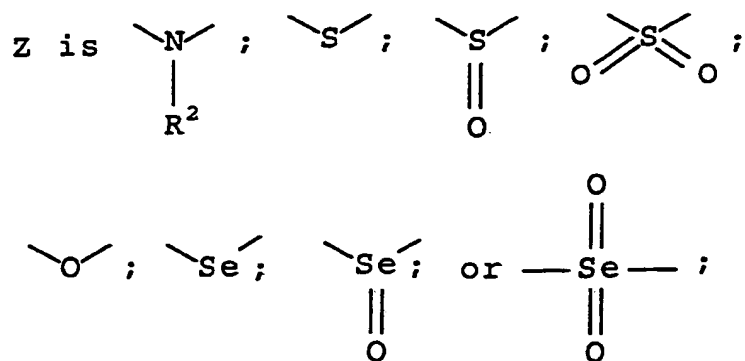
n and m individually are 0 or 1;

PUG is a photographically useful group;

25 x is 0, 1 or 2;

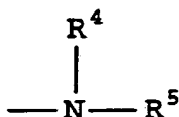
R^1 is unsubstituted or substituted alkyl;

Z is located at any ring position not adjacent to the ketocarbonyl group and;



substituted or unsubstituted alkyl or aryl or a
 5 photographic ballast group;

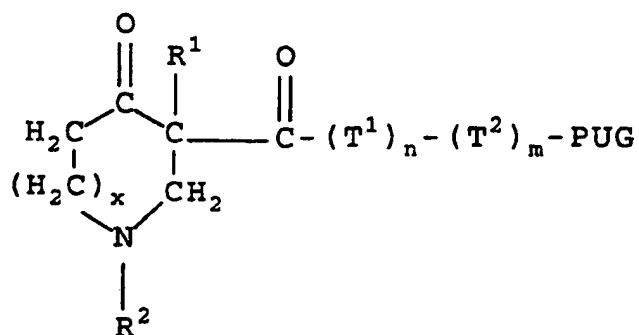
R^3 is unsubstituted or substituted alkyl, or
 aryl or



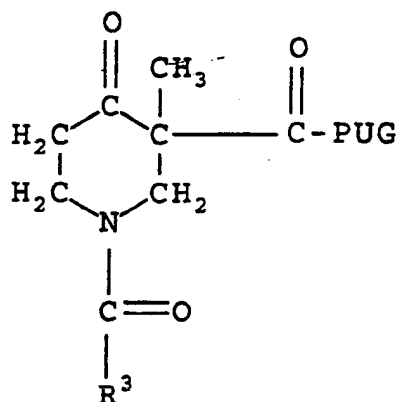
R^4 and R^5 individually are hydrogen, or
 10 unsubstituted or substituted alkyl or aryl;

R is substituted or unsubstituted alkyl or aryl
 or a photographic ballast group replacing a ring
 hydrogen; and Y is 0, 1, 2 or 3.

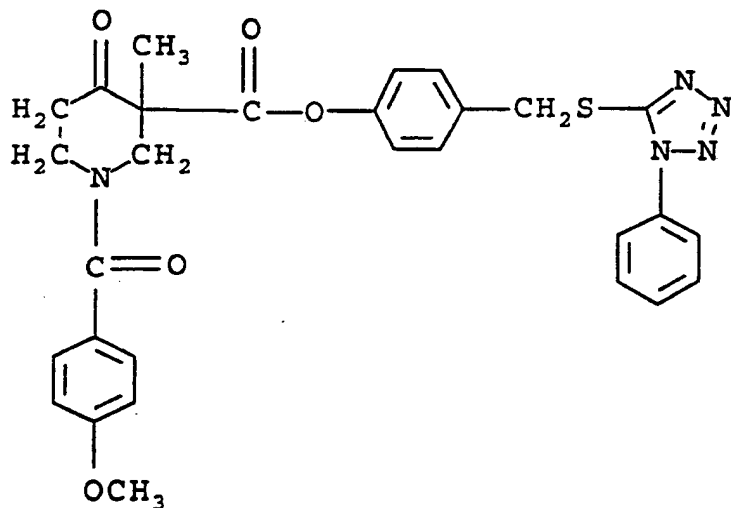
3. The elements of Claim 2 wherein the
 15 blocked compound is represented by the formula:

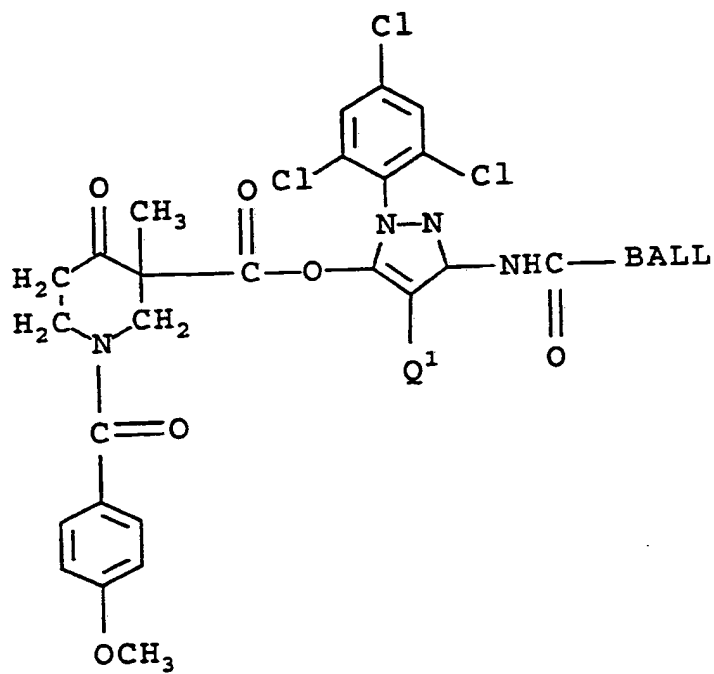
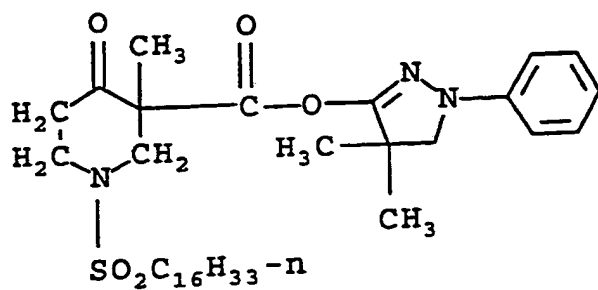


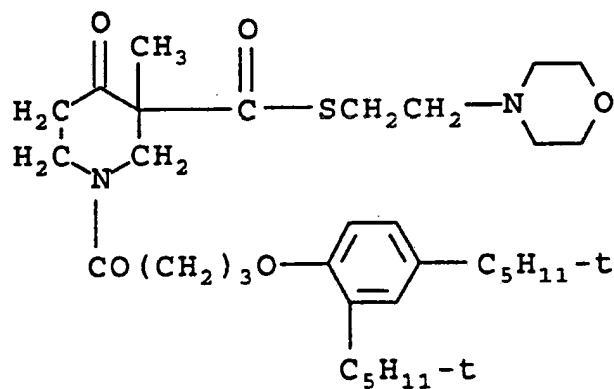
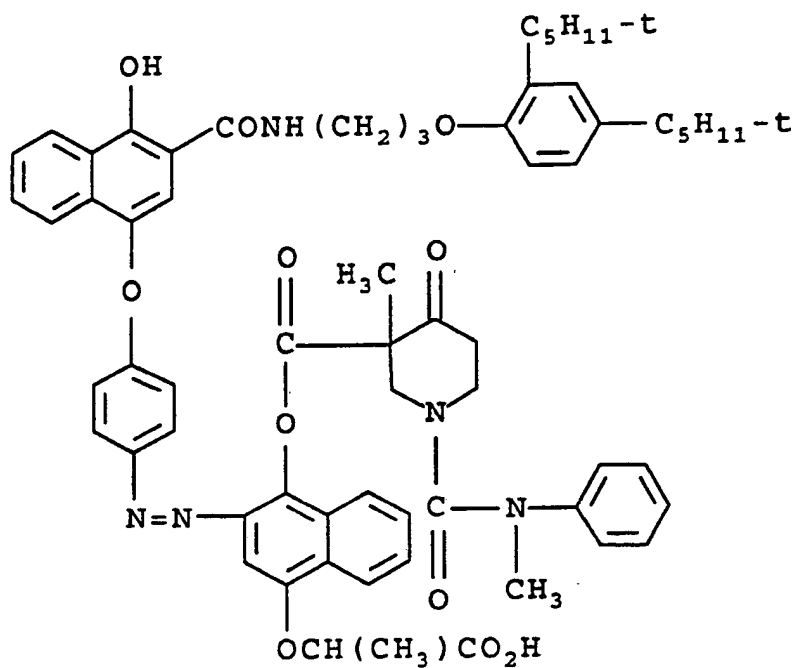
4. The element of Claim 3 wherein the blocked compound is represented by the formula:



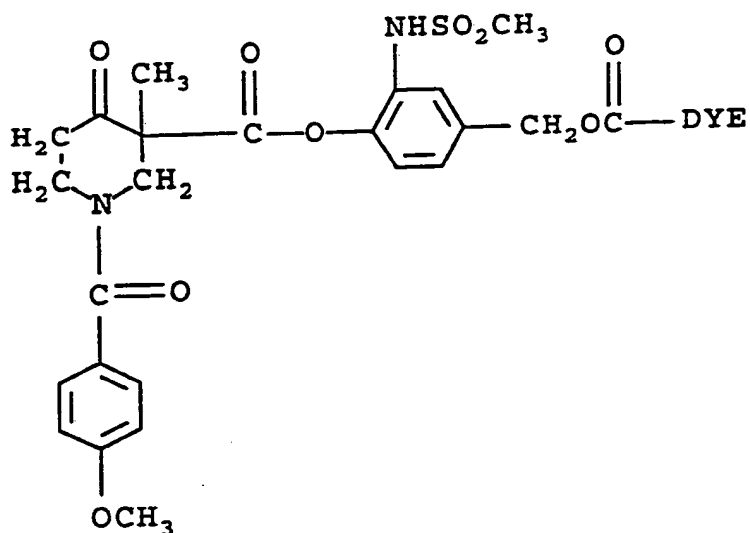
5. The element of Claim 3 wherein the blocked compound is one of the following:







5 or



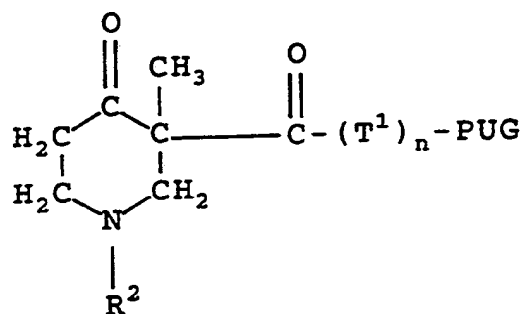
wherein

Q^1 is hydrogen or a coupling-off group;

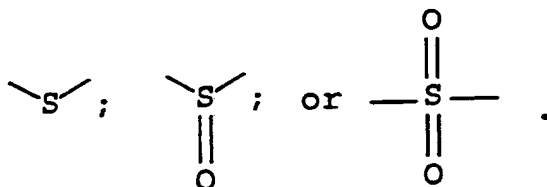
BALL is a ballast group; and

DYE represents the atoms completing a dye.

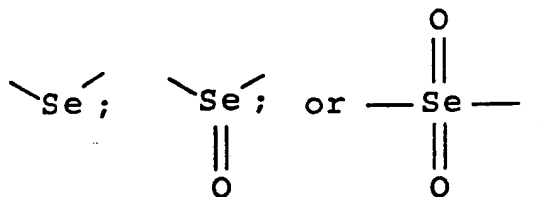
6. A photographic element as in Claim 1 wherein the blocked photographically useful compound is represented by the formula:



7. The element of Claim 2 wherein Z is



8. The element of Claim 2 wherein Z is



9. The element of Claim 2 wherein Z is -O-.

5 10. The photographic element of Claim 1
wherein the photographically useful group is a
coupler, dye, nucleating agent, development
accelerator, inhibitor releasing developer, color
developer, development restrainer, antifoggant,
10 bleach accelerator, bleach inhibitor, hardener,
silver halide solvent, or precursors thereof.

11. A process for developing a photographic
image comprising contacting an exposed photographic
15 element as defined in Claim 1 with a silver halide color
developing agent.

12. A blocked photographically useful compound
as defined in Claim 1.

INTERNATIONAL SEARCH REPORT

International Application :

PCT/US 92/06223

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 G03C7/305; C07D211/74; C07D207/24; C07D211/96
 C07D309/30; C07D335/02; C07D401/12; C07D401/14

II. FIELDS SEARCHEDMinimum Documentation Searched⁷

Classification System	Classification Symbols
Int.Cl. 5	G03C ; C07D

Documentation Searched other than Minimum Documentation
 to the Extent that such Documents are Included in the Fields Searched⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	EP,A,0 394 974 (EASTMAN KODAK COMPANY) 31 October 1990 see the whole document & US,A,5 019 492 cited in the application -----	1-12

⁹ Special categories of cited documents :¹⁰^{"A"} document defining the general state of the art which is not considered to be of particular relevance^{"E"} earlier document but published on or after the international filing date^{"L"} document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)^{"O"} document referring to an oral disclosure, use, exhibition or other means^{"P"} document published prior to the international filing date but later than the priority date claimed^{"T"} later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention^{"X"} document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step^{"Y"} document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.^{"A"} document member of the same patent family**IV. CERTIFICATION**

Date of the Actual Completion of the International Search 30 NOVEMBER 1992	Date of Mailing of this International Search Report 30.12.92
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer BUSCHA A.J. <i>Andreas Buscha</i>

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The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 30/11/92

EP-A-0394974	31-10-90	US-A-	5019492	28-05-91
		CA-A-	2013314	26-10-90
		JP-A-	2296240	06-12-90

